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EFFECT OF CHAIN EXTENSION ON RHEOLOGY AND TENSILE PROPERTIES OF PHB AND PHB-PLA BLENDS

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EFFECT OF CHAIN EXTENSION ON RHEOLOGY AND TENSILE PROPERTIES OF PHB AND PHB-PLA BLENDS

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Dedication

To Franz Pökler

Acknowledgments

Thanks to my supervisors, Dr. Pierre Carreau, Dr. Marie-Claude Heuzey and Dr. Nicole Demarquette for their financial support and direction, and for the opportunity to perform research for which I might be awarded a degree. This opportunity has allowed me to become a better engineer.

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Abstract

Poly(3-hydroxybutyrate), referred to as PHB, is a bacterially-synthesized and biodegradable polymer which is being considered as a substitute for non-biodegradable bulk polymers like polypropylene. PHB is naturally extremely isotactic and naturally has a very high degree of crystallinity, resulting in a stiff but brittle material. The stability of PHB crystals also means that the melting point of the polymer is approximately 170^{o}C, high with respect to similar polymers. For instance, the melting point of poly(4-hydroxybutyrate) is only 53^{o}C (Saito, Nakamura, Hiramitsu, & Doi, 1996). Above 170^{o}C, PHB is subject to a thermomechanical degradation mechanism, meaning that the polymer cannot be melted without degrading. One possible solution to the problem of degradation is to add a chain extender to the molten polymer to increase average molecular weight to counteract the molecular weight lost to degradation. In this work, a variety of chain extenders (Joncryl® ADR 4368-C, pyromellitic dianhydride, hexamethylene diisocyanate, polycarbodiimide) were compounded with a random copolymer of 98 mol% 3-hydroxybutyrate and 2 mol% 3-hydroxyvalerate (referred to as PHB) in concentrations ranging from 0.25% to 4%, to determine which chain extender functionality worked best with PHB. Molecular weight change was inferred from torque monitored during compounding, and from complex viscosity determined from parallel-plate rheology. None of the chain extenders changed the rate of degradation of PHB, although Joncryl increased the complex viscosity of the polymer. PHB was also blended with Poly(L-lactic acid), referred to as PLLA in PHB/PLLA ratios of 100/0, 75/25, 50/50, 25/75 and 0/100, to determine the effect of blending on the thermal stability of PHB. Again, thermal stability was determined by monitoring torque during compounding and by measuring complex viscosity through parallel-plate rheology. Blends in which PHB was the more abundant phase, as well as the 50% PHB/50% PLA blend continued to degrade, and the PLLA did not in these cases significantly increase complex viscosity. By contrast, the 25/75 PHB/PLLA blend had a complex viscosity equal to the neat PLLA blend, and both of the blends remained stable. All five blends were also produced with 1% Joncryl to observe the effect of Joncryl on the blends. In the 50/50 blend and the blends in which PLLA was the major component, complex viscosity increased by at least an order of magnitude, while in the 75/25 PHB/PLLA blend and the neat PHB blend, the effect of Joncryl was to increase complex viscosity only by a factor of 2. The effect of blending and of Joncryl on PHB-PLA blends was further investigated through uniaxial tensile stress testing of compression-

moulded samples of the blends, neat and with 1% Joncryl. The results showed an increase in tensile stress at yield and tensile strain at break for blends with the addition of Joncryl, although Young's modulus was somewhat diminished for these blends. In conclusion, chain extenders were not effective in reversing the effect of thermomechanical degradation, possibly because they do not change the resistance to bond rotation in PHB chains, or because they are not reactive with acrylates, although the exact cause has not been determined.

Résumé

Le poly(3-hydroxybutyrate), ou PHB, est un polymère biodégradable synthétisé par voie bactérienne. L'intérêt porté à ce polymère biodégradable est motivé par ses propriétés mécaniques, qui sont fort similaires à celles du polypropylène, un polymère non-biodégradable avec plusieurs applications commerciales. Actuellement, la substitution du polypropylène par du PHB est limitée par les propriétés physiques (?) de ce dernier qui le rendent difficile à traiter. Ces limitations sont liées au fait que le PHB est presque isotactique, ce qui signifie que sa cristallisation est fort favorisée. Cette cristallinité élevée rend le polymère rigide mais fragile, et augmente son point de fusion à 170^{o}C. Par comparaison, le point de fusion de poly(4-hydroxybutyrate) est de 53^{o}C. Ce point de fusion élevé complique le traitement du PHB, qui commence à se dégrader spontanément au-dessus de 170^{o}C, c'est-à-dire dès qu'il est fondu. Étant donné que le polymère doit être fondu afin d'être mélangé ou moulu, il est impossible d'éviter sa dégradation. Dans cette étude, le PHB est mélangé avec différents produits chimiques conçus spécialement pour augmenter le poids moléculaire des polyesters tels que le PHB. Ces produits chimiques sont appelés « chain extender », ou « allongeur de chaine », car ils réagissent avec les embouts des chaines polymériques pour produire une chaine allongée. Quatre allongeurs de chaine (le Joncryl ® ADR 4368-C, le dianhydride pyromellitique, le diisocyanate d'hexaméthylène, et le polycarbodiimide) ont été mélangés avec un copolymère aléatoire de PHB (98 mol%) et de poly(3-hydroxyvalerate) (2 mol%). La concentration d'allongeur de chaine dans le polymère a été variée entre 0.25% et 4% massique. L'évolution du poids moléculaire du polymère résultant de ces différents mélanges est déduite de la viscosité complexe, déterminée par rhéologie à plan parallèle. Il a été observé qu'aucun des allongeurs n'a permis de réduire le taux de dégradation du PHB, et que seul le Joncryl a entrainé une augmentation du poids moléculaire du polymère. Le PHB a également été mélangé avec du poly(L-acide lactique), ou PLA, pour des rapports PHB/PLA de 100/0, 75/25, 50/50, 25/75, et 0/100. Comme précédemment, la stabilité thermique a été déduite de la viscosité complexe. Lors de ces expériences, il a été observé que les mélanges riches en PHB (100% PHB/0% PLA, 75% PHB/25% PLA) ont continué à se dégrader au même taux que le PHB pur. Le mélange 50% PHB/50% PLA, quant à lui, a présenté un gain initial de viscosité complexe, mais a néanmoins continué à se dégrader au même taux que le PHB pur. Par contre, la viscosité complexe du mélange de 25% PHB/75% PLA était égale à celle du PLA pur. Ces cinq mélanges

ont ensuite été reproduits mais en présence de 1% massique de Joncryl dans le but d'étudier l'effet de l'allongement des chaines sur les caractéristiques du polymère. Il en a résulté que les mélanges 50% PHB/50% PLA, 25% PHB/75% PLA et 100% PLA présentaient une augmentation de viscosité complexe de plus de dix fois celle de leur homologue sans Joncryl. Cependant, le mélange 75% PHB/25% PLA n'a présenté une augmentation de sq viscosité complexe que de deux fois celle du mélange sans Joncryl. L'effet du Joncryl sur les propriétés mécaniques des mélanges de PHB et PLA a aussi été étudié par essai de traction uniaxial. Les résultats ont indiqué une augmentation de la contrainte au seuil d'écoulement et d'allongement à la rupture avec l'ajout de Joncryl, mais une diminution du module de Young. En conclusion, l'ajout d'allongeurs de chaines n'a qu'un effet marginal sur la dégradation du PHB.

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Chapter 1 Introduction

Poly(3-hydroxybutyrate), referred to as PHB, is a polymer in the polyhydroxyalkanoate (referred to as PHA) family which is synthesized by bacteria as an energy storage mechanism. PHB is completely biodegradable and has suitable mechanical properties for use as a bulk polymer. Recently, it has found use in a number of biomedical applications in part due to its biodegradability. Ideally, PHB or a similar biodegradable material would replace non-biodegradable polymers as the material of choice for packaging and cheap moulded articles, greatly reducing the amount of non-biodegradable waste production.

PHB had been produced industrially as its copolymer with hydroxyvalerate since the late 1960s, under the trade name Biopol®, by Zeneca, an ICI subsidiary. However, the demand for biodegradable polymers has only recently been great enough to support investment in this field: in the last decade, multi-ton PHA production has been announced by companies in the United States, Brazil, Europe and China. While production volumes are still relatively low, the market for PHAs is expected to increase over the next decade, with one estimate placing the PHA trade volume at 34,000 tonnes in 2018, up from 10,000 tonnes in 2013, with most demand located in Europe (Polyhydroxyalkanoate (PHA) Market, By Application (Packaging, Food Services, Bio-medical, Agriculture) & Raw Material - Global Trends & Forecasts to 2018, 2013).

In the United States, the biomaterials development company Metabolix partnered with agricultural giant Archer Daniels Midland to produce PHB under the trade name Mirel™ with a production capacity of 50,000 tons per year, starting in late 2010. Metabolix has since announced the capacity to produce PHA in transgenic tobacco and switchgrass plants. In 2012, Archer Daniels Midland ended any further commitment to the enterprise, forcing Metabolix to relocate production to a smaller, 10,000 ton per year facility in Spain with partner Antibióticos (Laird, 2012). In 2006, Procter and Gamble had announced a partnership with Kaneka Co. of Japan to develop a line of PHAs under the trade name Nodax®, but the venture was eventually halted. Meredian Inc. has since bought the assets to Nodax® and plans to produce 270 thousand tons per year. Kaneka, meanwhile, has announced plans to produce fifty thousand tonnes per year of PHBHx (Pollet & Avérous, 2011).

In Brazil, PHB Industrial produces 4000 tonnes per year of PHB homopolymer and copolymer with 12% hydroxyvalerate under the trade name Biocycle. In China, Tianan produces 2000 tonnes per year of PHB under the trade name Enmat, while Tianjin Green Bio-science Co. has partnered with DSM of the Netherlands to produce up to 10,000 tonnes per year of PHA (Pollet & Avérous, 2011).

Adoption of PHB as a commodity copolymer is currently constrained by two significant shortcomings. First, although the polymer is stiff, it becomes increasingly brittle as it ages. Packaging materials made from such a brittle material would be prone to cracking under even very small deformations. Second, the polymer is subject to a severe degradation mechanism that complicates processing. A significant amount of research has been invested in developing an improved PHB-based material, with some success. For instance, PHB-PHA copolymers are more ductile and can be processed at lower temperature while retaining biodegradability. A range of PHB blends with improved mechanical properties have also been reported, although PHB tends to blend best with chlorine-containing polymers which are not biodegradable and are often toxic.

In this work, an attempt is made to address both the degradation and brittleness of PHB through the use of so-called chain extender compounds – multifunctional macromolecules designed to react with polyesters like PHB. Four chain extenders were selected: Joncryl®, an oligomer with several epoxide groups; polycarbodiimide, referred to as PCDI; hexamethylene diisocyanate, referred to as HMDI; and pyromellitic dianhydride, referred to as PMDA. These specific chain extenders were selected to represent a wide array of functionality.

Chain extenders were tested at three different concentrations, to determine which chain extender worked best, and at which concentration it had the greatest effect. The goal was to develop a method which maintained stable molecular weight at temperatures where PHB would be expected to degrade. PHB was then blended with another biodegradable polymer with two objectives: first, to develop a biodegradable material with suitable tensile properties for use as a commodity polymer; second, to determine the effect of a chain extender on the properties on the blend.

Although other biodegradable polymers may be suitable for blending with PHB, PLA has been selected as a polymer with which to blend PHB based on the success reported in literature.

This work also includes a simple method to monitor degradation in real time from complex viscosity. This method, adapted from previous work, proved necessary because of the difficulty encountered in dissolving the grade of PHB used which made chromatography impossible.

Chapter 2 Literature Review

2.1 History of PHB and its Shortcomings as a Commodity Polymer

2.1.1 Brief History of PHB

First observed in 1903 as lipid-like sudanophilic inclusions in Azobacter chroococcum (Meyer, 1903) soluble in chloroform (Stapp, 1924), the polymer was not identified as poly(3-hydroxybutyrate) until 1927 in cells of Bacillus megaterium (Lemoigne, 1927). Over the subsequent decades, PHB was found in a range of gram-negative bacteria, and its role in the metabolism of these microbes was characterized: the polymer is produced as a storage mechanism in environments where nitrogen supply was insufficient, fulfilling a metabolic role similar to that of starch or glycogen (Williamson & Wilkinson, 1958) (Macrae & Wilkinson, 1958) (Doudoroff & Stanier, 1959). In the late 1960s, several other bacterially-produced polyhydroxyalkanoates (PHAs) were discovered (Wallen & Rohwedder, 1974) (Findlay & White, 1983) (De Smet, Eggink, Witholt, Kingma, & Wynberg, 1983) (Lageveen, et al., 1988). At present, at least 125 hydroxyacids have been identified as monomers for bacterially-synthesized polymers (Rehm & Steinbüchel, 1999).

Interest in PHB stems from the fact that, as shown in Table 2.1, extracted PHB has comparable mechanical properties to polypropylene (Sudesh, Abe, & Doi, 2000) (Avella, Martuchelli, & Raimo, 2000), while being biodegradable and produced from renewable feedstock. It wasn't until 1962 that the polymers' potential in this capacity was realized (Baptist, 1962), but within 5 years industrial production of the polymer had already begun (Holmes, 1967).

2.1.2 Practical Shortcomings of PHB, and Their Relationship to Crystallinity

While PHB is remarkably stiff, it is not very extensible. This because bacterially synthesized PHB is almost completely isotactic, allowing easy crystallization. While the polymer is completely amorphous (Barnard & Sanders, 1989) (Kawaguchi & Doi, 1990) (Amor, Rayment, & Sanders, 1991) in vivo, when isolated its degree of crystallinity can exceed 80% (Holmes, 1967) (Anderson & Dawes, 1990). At such high degrees of crystallinity PHB tends to crack easily, precluding its use in applications where some flexibility is desirable. Compounding this shortcoming is the fact that PHB becomes increasingly brittle as it ages due to a secondary crystallization mechanism which occurs at room temperature, putting stress on primary crystal

spherulites leading to the development of microscopic fractures (Martinez-Salazar, Sanchez-Cuesta, Barham, & Keller, 1989). This aging process can be prevented by annealing (De Koning & Lemstra, 1993) (DeKoning, Scheeren, Lemstra, Peeters, & Reynaers, 1994) (Kurusu, Demarquette, Gauthier, & Chenal, 2012), presumably because of the increased mobility available at higher temperature which allows crystal spherulites to rearrange themselves in the most thermodynamically stable configuration.

Table 2.1: Comparison of PHB and isotactic polypropylene (Avella, Martuchelli, & Raimo, Review: Properties of blends and composites based on poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-hydroxyvalerate) (PHBV) copolymers, 2000) (Mark, Gaylord, Bikales, (eds.), 1964) (Brandup, Immergut, (eds), 1975)

Polymer	Melting Temperature (^oC)	Glass Transition Temperature (^oC)	Tensile Strength (MPa)	Elongation (%)	Elastic Modulus (GPa)
PHB	175	9	45	4	3.8
i-polypropylene	174	-17	30	10	1.5

Another consequence of the high degree of crystallinity typical of PHB is that relative to other PHAs it has an elevated melting temperature. For instance, poly(4-hydroxybutyrate) has a melting temperature of 53^{o}C (Saito, Nakamura, Hiramitsu, & Doi, 1996) and poly(3-hydroxyvalerate) has a melting temperature of between 103^{o}C and 108^{o}C (Van de Velde & Kiekens, 2002) while the melting temperature of poly(3-hydroxybutyrate) is between 170^{o}C and 175^{o}C (Sudesh, Abe, & Doi, 2000). The high melting temperature means that PHB must first be heated to between 180^{o}C and 190^{o}C in order to be processed. At this temperature, PHB degrades spontaneously through the so-called thermomechanical degradation mechanism characteristic of all 3-hydroxyalkanoate polymers.

This reaction was studied in depth by Grassie et al. in a set of three papers identifying the mechanisms through which PHB degraded as well as the resulting products. Among other things, these articles demonstrated that: degraded PHB ultimately took the form of 2-butenoic acid, the rate of degradation increased with temperature, and degradation could be modeled by a zeroth-order rate equation (Grassie & Murray, 1984) (Grassie & Murray, 1984) (Grassie & Murray, 1984). More recent articles on this degradation mechanism agree that the

thermomechanical degradation mechanism is most likely a McLafferty rearrangement, shown in Figure 2.1 below.

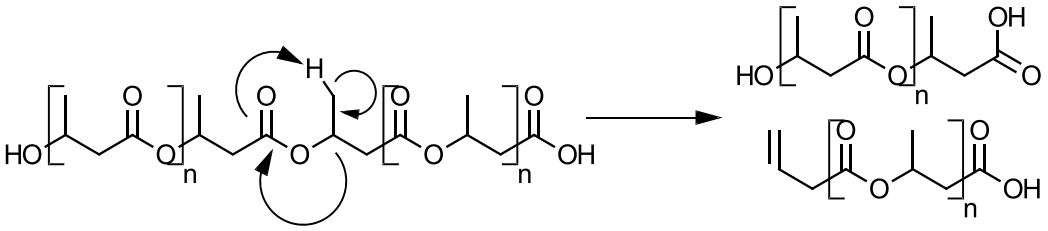

Figure 2.1: Thermomechanical degradation mechanism of PHB

2.1.3 Characterizing Thermomechanical Degradation

Using the same rate equation as Grassie, Melik and Schechtman were able to correlate torque in a masterbatch mixer with degradation rate, and were able to determine a rate constant dependent on shear rate and temperature (Melik & Schechtman, 1995). Equation 2.1 shows the degradation rate in terms of the instantaneous number average M_{nt}, the original number average M_{no}, and a rate constant k.

Equation 2.1: Degradation rate of PHB

$$\frac{1}{M_{nt}} - \frac{1}{M_{no}} = kt$$

A number of researchers have attempted to characterize PHB degradation via thermogravimetry (Liu Q.-S. , Zhu, Wu, & Qin, 2009) (Hablot , Bordes, Pollet, & Avérous, 2008) (Hong, Lin, & Lin, 2008). While expedient, this is not an accurate method for monitoring the reaction. Aoyagi et al. monitored the change in number average molecular weight and the change in mass of a sample of PHB during isothermal degradation at 170^{o}C (Aoyagi, Yamashita, & Doi, 2002). The result of this experiment, shown in shows that even when no weight change occurs, the molecular weight of PHB is degrading. Clearly, thermogravimetric analysis does not present an accurate picture of degradation.

There is a significant amount of evidence from both rheology and chromatography, that the molecular weight distribution does not change as a result of degradation (Aoyagi, Yamashita, & Doi, 2002) (Yamaguchi & Arakawa, 2006). Consequently, the extent of degradation can be monitored from calculations of average molecular weight, which can be determined from

rheology. The relationship between viscosity of a molten aliphatic polymer and its average molecular weight can be modeled with a power-law relationship, shown in Equation 2.2, where α is almost always 3.4 for straight-chain polymers with no branching. Here, A is a proportionality constant, M_W refers to molecular weight and η^* to viscosity.

Equation 2.2: Empirical relationship between molecular weight and viscosity

$$\boldsymbol{\eta = A{M_W}^{\alpha}}$$

The complex viscosity (η^*) of a molten polymer can be easily and accurately determined from oscillatory shear, given a few conditions. First, the amplitude of the oscillating shear must be small enough to be within the linear viscoelastic region of the polymer, meaning small enough that the response to strain is not a function of past strain. Second, the complex viscosity under oscillating strain must follow the same trend as viscosity under steady strain (η) at a shear rate ($\dot{\gamma}$) numerically equal to the frequency of the oscillating strain (ω). This second condition is also called the Cox-Merz rule, and has previously been validated for PHB (Park, Lim, Shin, Choi, & Jhon, 2001).

Equation 2.3: Cox-Merz rule

$$\lim_{\dot{\gamma}\to\omega} \eta(\dot{\gamma}) = |\eta^*(\omega)|$$

Degradation can also be monitored in real time during processing. Melik and Schechtman demonstrated a method to monitor degradation during compounding by inferring molecular weight from compounding torque. If the viscosity of a chemically stable molten polymer is assumed to vary with temperature according to the Arrhenius relationship (Equation 2.4) then a linear relationship should exist between the logarithm of viscosity and the inverse of absolute temperature. The same article demonstrated that compounding torque output could be substituted for viscosity to yield Equation 2.5, where $\hat{T}$ represents torque and T represents temperature, E_a represents some activation energy, R the ideal gas constant and η_0 a reference viscosity (Melik & Schechtman, 1995).

Equation 2.4: Arrhenius temperature-viscosity relationship for liquid polymer

$$\eta(T) = \eta_0 \exp\left(\frac{E_a}{RT}\right)$$

Equation 2.5: Compounding torque as a function of temperature for an inert liquid polymer

$$\ln \hat{T} = \frac{E_a}{RT} + \ln \hat{T}_0$$

In a similar vein to the work of Melik and Schechtman, other researchers have developed models which allow PHB degradation to be estimated from typical processing parameters. In one such study, degradation in injection moulding was found to be very highly correlated to injection pressure and injector capillary diameter (Leroy, Petit, Audic, Colomines, & Deterre, 2012), while in another experiment, injection parameters were successfully correlated with tensile mechanical properties of PHB as well as molecular weight (Renstad, Karlsson, & Albertsson, 1997).

Two shortcomings have so far been outlined for PHB: thermomechanical degradation and brittleness. If PHB is to become a useful commodity polymer these shortcomings must be addressed, through the development of processing methods which avoid degradation, and through modifications which prevent the formation of microfractures. Significant effort has already been devoted to this goal, as shown by the body of literature on the subject. These efforts are discussed in the following section.

2.2 Strategies to Improve PHB

In the previous section, the two primary shortcomings of PHB as a commodity polymer are discussed. Both are related to the thermodynamic favorability of PHB crystallization. With respect to thermomechanical degradation, the stability of PHB crystals elevates the melting point, so that the polymer cannot be melted without degrading – if the melting point could be depressed, degradation could be avoided. The brittleness of PHB is related to flaws in the crystalline phase of the polymer, and would almost certainly be mitigated by a reduction in crystallization.

This section discusses methods to modify PHB through copolymerization and through blending with the goal of producing a material free of, or at least less hampered by, the shortcomings of the homopolymer. It should be noted that much of this section is at most tangentially related to the present work, and is included for the sake of background.

2.2.1 PHB-PHA Copolymerization to Diminish Crystallinity

One method to reduce the favorability of crystal formation in PHB is to copolymerize it. Often, PHB is copolymerized with other hydroxyalkanoates, because they can be produced microbially through essentially the same process which produces PHB by subtly modulating growth conditions and feedstock composition (Sudesh, Abe, & Doi, 2000), and because PHA copolymers are also biodegradable. The most common PHA copolymers are probably poly(3-hydroxybutyrate-co-3-hydroxyvalerate), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), and poly(3-hydroxybutyrate-co-3-hydroxyoctanoate), although many others exist.

Almost all PHA comonomers inhibit growth of PHB spherulites by coordinating with the surface of growing crystals, preventing amorphous PHB from joining the crystal. For example, PHB spherulite growth was shown to drop by a factor of 4 when PHB was copolymerized with 27% 3-hydroxypentanoate (Ichikawa, et al., 1996). This inhibition is also manifested in depressed heat of fusion, temperature of fusion, glass transition temperature and degree of crystallinity for P(HB-HA) copolymers, which have all been reported in response to increased HA comonomer content (Shimamura, Scandola, & Doi, 1994) (Doi, Kitamura, & Abe, 1995) (Matsusaki, Abe, & Doi, 2000). Lamellar thickness has also been demonstrated to decrease with increasing HA comonomer fraction (Abe, Doi, Aoki, & Akehata, 1998) (Abe, et al., 1999), and a linear relationship (Figure 2.2) has been determined between melting temperature and the inverse of

lamellar thickness (Orts, Marchessault, & Bluhm, 1991). In some cases, secondary crystallization has been reported, such as when PHB-co-HHx was found to form relatively thin (3-4 nm thickness) crystal lamellae during storage at room temperature. These crystals disappeared when the material was heated above 110°C (Abe, et al., 1999). It is supposed that these crystals are grown from segments of PHB which are too short to join lamellae during fusion without incorporating the comonomer.

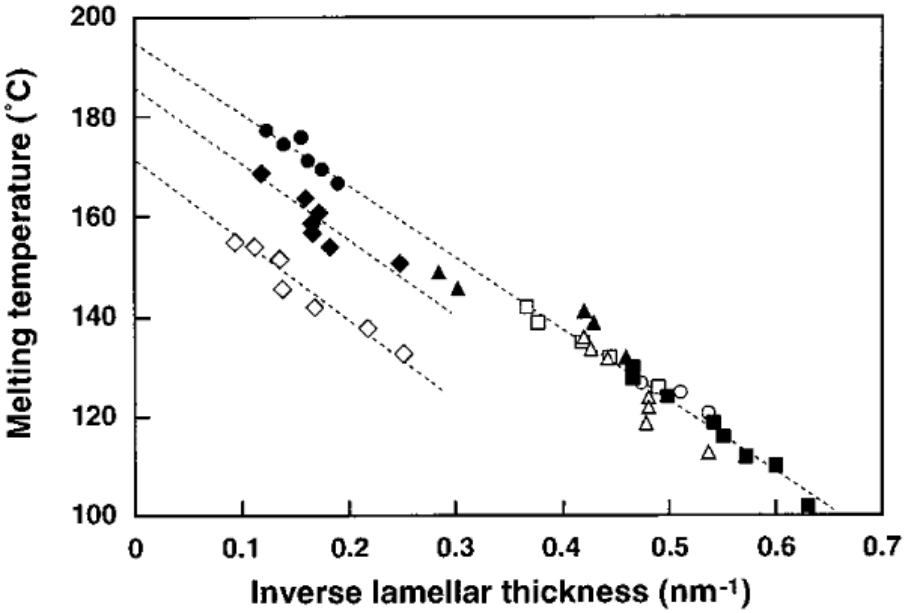

Figure 2.2: Melting temperature as a function of inverse lamellar thickness for PHB-HA copolymers: [Black Circles: Poly(3-hydroxybutyrate); Black Diamonds: Poly(3-hydroxybutyrate-*co*-6%-3-hydroxyvalerate); White Diamonds: Poly(3-hydroxybutyrate-*co*-16% hydroxyvalerate); White Circles: Poly(3-hydroxybutyrate-*co*-8%-3-Hydroxyhexanoate); Black Triangles: Poly(3-hydroxybutyrate-*co*-8%-4-hydroxybutyrate); White Triangles: Poly(3-hydroxybutyrate-*co*-10%-4-hydroxybutyrate); Black Squares: Poly(3-hydroxybutyrate-*co*-10%-6-hydroxyhexanoate); White Squares: Poly(3-hydroxybutyrate-*co*-5%-lactide)].
Graphic reproduced from Abe et al. [42]

An exception to the trend for PHB-PHA crystallization can be seen in Figure 2.2, where two sets of samples do not follow the same trend as the other copolymers. Both of these samples are copolymers of 3-hydroxybutyrate and 3-hydroxyvalerate, referred to as PHBV, and in both cases the lamellar thickness is in the same range as the PHB homopolymer while melting temperature is depressed (Abe, Doi, Aoki, & Akehata, 1998). This is because (unlike other hydroxyacid comonomers) 3-hydroxyvalerate can incorporate itself in PHB homopolymer crystal lamellae, albeit as a defect causing a diminished heat of fusion for the crystal. Also unlike other HA comonomers, because PHB and PHV crystal lattices are isodimorphic, meaning the crystal

structures of the two copolymers have almost identical characteristics (Orts, Marchessault, & Bluhm, 1991). For HV comonomer fractions below 20%, the crystal lattice as determined by electron diffraction is virtually the same as that of PHB homopolymer (Marchessault, et al., 1988), although degree of crystallinity drops rapidly as a function of HV. Between 20% and 30% HV content, PHB crystals begin to exhibit irregular or 'bumpy' surfaces (Mitomo, Barham, & Keller, 1987), and the degree of crystallinity is significantly depressed, reaching a minimum at 34% HV (Orts, Marchessault, & Bluhm, 1991). At the minimum crystallinity, the copolymer is significantly different from the homopolymer: melting temperature is 97^{o}C as opposed to 175^{o}C for PHB; glass transition changes from 9^{o}C to -9^{o}C, tensile strength drops from 45MPa to 18MPa; elongation increases from 4% to 970%; elastic modulus drops from 3.8GPa to 1.2GPa (Avella, Martuchelli, & Raimo, 2000). In sum, the stiff, brittle homopolymer is converted to a ductile copolymer.

Copolymers of hydroxybutyrate with either hydroxyhexanoate (HHx), hydroxyheptanoate (HHp) or hydroxyoctanoate (HO) are often referred to as medium-chain-length, or MCL, copolymers, referring to the length of branching chains, which are not short enough to be incorporated in hydroxybutyrate crystals but not long enough to affect flow properties (Sudesh, Abe, & Doi, 2000). The ductility of MCL PHA copolymers is exemplified by the properties of a material in which 94% of the repeat units were HB, with the remaining 6% made up of a mixture of MCL 3-hydroxyacids. This material was shown to have properties similar to LDPE (Matsusaki, Abe, & Doi, 2000). Similarly, films of between 10% and 12% HHx or HO copolymerized with PHB were shown to have comparable Young's modulus to HDPE (Satkowski, et al., 2001).

To conclude, copolymerization of PHB with other hydroxyacids can result in significant improvements to mechanical and thermal properties. The copolymer can be made to be tougher, more ductile and to have a lower melting temperature than the PHB homopolymer, due primarily to disruption of PHB homopolymer crystal growth.

2.2.2 Blending of PHB to Improve Mechanical Properties

PHB properties are also improved when it is blended with other polymers. Blending is often cheaper than copolymerization, and the properties of the blend can easily be modulated through changes in composition. However, only a handful of polymers are compatible with PHB, most of which are non-biodegradable or toxic.

Like most polyesters, PHB is more likely to be compatible with hydrogen-bond donors. This explains why PHB forms miscible blends with chlorine-containing polymers, such as polyepichlorohydrin (PECH) (Dubini Paglia, et al., 1993) (Sadocco, Canetti, Seves, & Martuscelli, 1993) and polyvinyl chloride (PVC) (Dave, Ashar, Gross, & McCarthy, 1990) , which are thought to form hydrogen bonds between chlorine-adjacent carbons and acyl oxygen on PHB (Pouchlý & Biroš, 1969) (Holmes, Willmouth, & Newton, 1983). Hydrogen bonding is also partly responsible for the miscibility between PHB and polyvinyl acetate (PVAc) (Greco & Martuscelli, 1989) (Kumagai & Doi, 1992), but does not explain why PHB is miscible with fluorine-containing polyvinylidene fluoride (PVDF) (Marand & Collins, 1990), and low molecular weight (below 50 kDa) polyethylene oxide (PEO) (Kumagai & Doi, 1922) (Avella & Martuscelli, 1988) since no hydrogen bonding is possible for these polymers. In such cases miscibility is attributed to dipole-dipole interaction rather than hydrogen bonding (Avella, Martuscelli, & Raimo, 2000). Dipole-dipole interaction is a much weaker phenomenon than hydrogen bonding and is strongly sensitive to geometrical factors, possibly explaining why polymethylene oxide (Avella, Martuscelli, Orsello, Raimo, & Pascucci, 1997) and polypropylene oxide (Avella, Martuscelli, & Raimo, 2000) are immiscible with PHB (in contrast with polyethylene oxide) (Avella, Martuscelli, & Raimo, 2000). Polymethyl methacrylate (PMMA)-PHB blends containing no more than 20 wt% PHB are reported to be miscible, forming single-phase glasses with composition-dependent glass transition. When PHB content is greater than 20 wt%, the blend separates into two phases, one containing PHB exclusively and the other containing 20% PHB and 80% PMMA (Lotti, Pizzoli, Ceccorulli, & Mariastella, 1993).

Although miscible blends can be produced with PHB, co-crystallization has so far not been reported with PHB and any non-PHA polymer. Notwithstanding, miscible polymers can have a significant effect on PHB crystallization. In PHB-PEO blends for instance, crystallization is a complex phenomenon that is dependent upon thermal history, crystallization conditions and

crystallization rate (Avella, Martuscelli, & Raimo, 1993). If PHB crystallization occurs first, PEO crystals will not form spherulites. Instead, PEO crystals appear to develop in the interlamellar regions of PHB crystals, forming fibrillar structures containing both types of crystals (Sharples, 1972). In PECH-PHB blends, crystallization is not as complex, but the addition of PECH reduced the rate at which PHB crystals grew (Dubini Paglia, et al., 1993). In PMMA-PHB blends, the 20/80 PHB/PMMA phase may inhibit crystallization (Lotti, Pizzoli, Ceccorulli, & Mariastella, 1993).

Although a bevy of articles have been published on crystallization and morphology of miscible PHB blends, relatively little has been reported about the mechanical properties of these blends. Tensile testing is only reported for the PECH-PHB blend, which was shown to have improved tensile strength compared to PHB, possibly due to the diminished crystallization and attractive forces between the two polymers (Kumagai & Doi, 1992). Mechanical properties have, however, been explored for PHB-rubber blends (Abbate, Martuscelli, Ragosta, & Scarinzi, 1991) (Avella, et al., 2003), and blends of PHB and styrene copolymers (Dave, Ashar, Gross, & McCarthy, 1990). When blended with polystyrene and polystyrene-acrylonitrile, little or no compatibility was reported and tensile properties were not improved, except for the 20 wt% PS/80 wt% PHB blend. A number of rubber – PHB blends in a ratio of 20 wt% rubber/80 wt% PHB, shown in Table 2.2, had improved elongation at rupture despite diminished Young's modulus and stress at rupture (Abbate, Martuscelli, Ragosta, & Scarinzi, 1991).

Blend properties can be improved by reactive blending, where a chemical reaction occurs during processing to improve compatibility. Reactive blending of PHB and PHBV with 30 wt% acrylate rubber improved impact strength relative to PHB alone (Avella, et al., 2003). When PHBV was blended with an epoxidized rubber and annealed at temperatures between 220^{o}C and 235^{o}C, PHBV reacted with the epoxide to form chemical bonds with the rubber. As a result, the formerly immiscible blend became miscible, although after being grafted in such a way PHBV was unable to crystallize (Han, Ismail, & Kammer, 2004). Reactive blending can also be accomplished through the addition of peroxides. For instance, dicumyl peroxide (DCP) was used to increase the compatibility between PHB and poly(ε-caprolactone), referred to as PCL, although the mechanical properties of the blend were only improved for the 70 wt% PCL/30% wt% PHB with 5% DCP (Immirzi, Malinconico, Orsello, Portofino, & Volpe, 1999).

Table 2.2: Young's modulus, stress and strain at rupture for 80% PHB/20% rubber blends

Sample	Young's Modulus (GPa)	σR (MPa)	ER (%)
PHB	2.1	290	1.5
PHB-EPR	1.5	170	2.0
PHB-EVA	1.6	175	2.0
PHB-EVOH	1.7	185	3.0
PHB-EPR-g-DBM	1.6	175	4.0
PHB-EPR-g-SA	1.6	180	6.5

PHB has also been blended with plasticizers, potentially creating a tougher, more extensible material. Bisphenol A was found to reduce the melting temperature and crystallization rate of PHB due to hydrogen bonding between the two components (Fei, et al., Modified poly(3-hydroxybutyrate-co-3-hydroxybutyrate) using hydrogen bonding monomers, 2004) (Fei, et al., Quantitative FTIR study of PHBV/bisphenol A blends, 2003). PHBV was also plasticized, with epoxidized soybean oil, dibutyl phthalate (DBP) and triethyl citrate (TEC), at 20 wt% in films pressed at 190^{o}C. While epoxidized soybean oil showed an improvement in elongation at break, it was not as effective as DBP and TEC in this regard. Impact testing showed improved toughness for all three blends, especially the blend containing DBP (Choi & Park, 2004).

The improved mechanical properties of PHB blends often come at the expense of biodegradability, one of the chief assets of PHB. Biodegradable PHB blends have been developed with cellulose derivatives, starch, PCL and PLA. When blended with cellulose from wood fibers, the polymer had improved strength and stiffness but was more brittle (Gatenholm, Kubát, & Mathiasson, 2003). Similarly, when blended with steam-exploded wheat straw fibers, mechanical properties were improved, probably due to hydrogen bonding between PHB and straw fibers in the amorphous phase (Avella, et al., 1993). PHB is also miscible with cellulose acetate butyrate (CAB) at compositions between 5% and 50% PHB, and cellulose acetate propionate (CAP) at compositions between 5% and 60% PHB (Scandola, Ceccorulli, & Pizzoli, 1992). In these ranges of composition, crystallization was completely inhibited and the material formed a transparent glass. A blend of PHBV and CAB was found to have decreasing elastic modulus and tensile strength as PHBV content increased from 20% to 50%, although tear strength and elongation at break increased. At PHBV loading above 50% the cellulose acetate esters were only partially miscible, and the elongation at break drops while elastic modulus,

tensile strength and tear strength continue to increase. A synergy in tensile properties between the two components was found at 70 wt% PHB/30 wt% CAB (Lotti & Scandol, 1992). Addition of starch without any other bonding agent made PHB more brittle, with decreased strain and stress to break (Koller & Owen, 1999). However, PEO-coated starch greatly improved the tensile properties of PHBV (Shogren, 1995).

2.2.3 Conclusions: Lessons from PHB Research, and Motivation for the Present Work

In this section, a review of efforts to develop an improved PHB-based material has been provided. Some remarkable discoveries are reported: the depressed melting point of PHB-PHA composites means that the polymer can be processed without degrading; miscible blends of PHB have been identified, and they promise to have improved mechanical properties; finally, degradable composites of PHB and organomodified cellulose have been developed.

While the progress made to this point on a PHB-based biodegradable commodity polymer is salutary, it has yet to achieve its goal. Most of the research was performed using solvent-cast films as opposed to extruded or compounded polymer. The former method allows better control of reaction conditions but is not representative of the conditions encountered in conventional polymer processing. Also, only a handful of articles discuss treatments of PHB with the stated aim of mitigating the effects of degradation. Instead, most articles either try to avoid degradation entirely by reducing the melting temperature or suggest methods to improve mechanical properties in response to degradation.

These conclusions suggest two motivations for the current work:

1. a method by which PHB degradation might be reduced or halted completely has yet to be found, and has not been explored to any great extent;
2. only a small fraction of research on PHB-based materials is done in conditions comparable to conventional polymer processing. This will be discussed further at the end of the literature review.

2.3 PHB-PLA Blends

In the last section, biodegradable PHB-based blends were briefly touched upon. The environmental benefit of biodegradability is well understood, and consequently a great degree of interest is invested in any such blends. Until recently, the topic has not been explored to any great extent, leading to a second objective for this work: the study of PHB-PLA blends with the aim of developing a biodegradable material with novel properties.

2.3.1 Introduction to PLA

PLA refers to either poly(lactic acid) or poly(lactide), depending on the monomer used. The polymer structure is the same regardless, but the distinction exists due to differences in the polymerization mechanisms through which monomers are converted to PLA. Lactic acid is heated under reduced pressure to promote polycondensation, with the degree of polymerization dictated by the amount of water removed from the reaction mixture. Polylactide is synthesized through a catalyzed ring-opening reaction from lactide dimer. Many synthesis pathways have been found, through cationic, anionic and radical mechanisms (Kricheldorf, Syntheses and application of polylactides, 2001) (Kricheldorf, Anionic polymerization of L-lactide in solution, 1990) (Kricheldorf & Dunsing, 8. Mechanism of the cationic polymerization of L,L-dilactide, 1986).

When polymerized to high molecular weight, PLA is a stiff, transparent amorphous polymer. When PLA is racemic, it is almost devoid of crystallinity (Gupta & Kumar, 2007). Annealing can increase the degree of crystallinity, although annealing at a temperature much above 120^{o}C significantly reduces extension and stress at break (Tsuji & Ikada, 1995). In addition to its problems with crystallinity, PLA has a low heat distortion temperature which can be improved with blending.

2.3.2 PHB-PLA Blends: Literature Review

A number of researchers have recently experimented with PHB-PLA blends with some success: well-dispersed droplets of PHB in a PLA matrix improved the heat deflection temperature, tensile strength and foam nucleation density relative to PLA alone (Zhang & Thomas, 2011) (Richards, Rizvi, Chow, & Naguib, 2008). Some interesting results have also been reported for cold-drawn, solvent cast PHB-PLA blend films (Park, Doi, & Iwata, 2004).

In a ratio of 75% PLA to 25% PHB, droplets of PHB improved the heat distortion temperature, elongation and tensile stress at break of the blend relative to 100% PLA. The droplets were also demonstrated to nucleate PLA crystallization with appropriate annealing (Zhang & Thomas, 2011). When Nodax™ (a copolymer of PHB with mcl PHA) was blended as the minor phase in a 90%/10% ratio with PLA, the energy-to-break of the blend greatly improved over 100% PLA (Noda, Satkowski, Dowrey, & Marcott, 2004). Blended in a weight ratio of 1:1, the occurrence of PLLA crystals was found to lower the peak crystallization temperature of PHB and change its crystallization mechanism – whereas the Avrami coefficient for PHB is normally 2.5, a coefficient of 5 was plotted for PHB crystallization in the blend, although a subsequent secondary PHB crystallization had an Avrami coefficient of 2.5 (Zhang, et al., 2006). When PLA is saturated with supercritical carbon dioxide, PHB droplets act as a nucleating agent for heterogeneous bubble nucleation, producing improved foams (Richards, Rizvi, Chow, & Naguib, 2008). Finally, films of PHB-PLLA were found to have increased crystallinity when they were drawn uniaxially at 60^{o}C for blends with a PLLA matrix, and at 2^{o}C for blends with a PHB matrix. The drawn films also had greater tensile strength, Young's modulus and elongation at break (Park, Doi, & Iwata, 2004).

Although PHB and PLA are immiscible, interesting interaction has been reported in blends containing less than 25% PHB by weight. In this range of composition, PLLA glass transition temperature reached a minimum of 44^{o}C, down from 60^{o}C for neat PLLA, while PLLA crystallization reached a minimum of 86^{o}C from over 120^{o}C for the neat polymer (Hu, Sato, Zhang, Isao, & Ozaki, 2008). Improved mechanical properties were also associated with transparent PLLA-PHB blends, suggesting that if PHB crystallization was inhibited the resulting material would be tougher, and that absence of crystallization was due to an interaction between PLLA and PHB (Noda, Satkowski, Dowrey, & Marcott, 2004). Improved tensile strength has been reported in this region, although there is no indication of crystallization effects in this case (Zhang & Thomas, 2011).

To conclude, some mechanical synergies have been reported in PHB-PLA blends along with some improvement in heat distortion temperature. Both improvements are reported when PLA is the major component and seem to be related to the crystallization of PHB droplets. PHB has also been reported to have some interaction with PLA when the former is at very low concentrations.

Therefore, the investigation of PHB will not just be limited to reducing degradation but to blending of PHB with PLA in the pursuit of a blend with synergistic properties.

2.4 Chain Extenders

As mentioned previously in this review, despite the advances made towards a viable PHB-based polymer, no solution has yet been found for to thermomechanical degradation. A solution to thermomechanical degradation is still a valuable and as-yet unattained objective. Fortunately, the problem of thermomechanical degradation may be solved through the use of chain extenders.

Chain extenders are a class of additives used to modulate the mechanical properties of polyesters. They are characterized as being reactive with functional groups forming the ends of polyester chains (alcohols and carboxylic acids) and having at least two reactive sites. When mixed with a polyester, a chain extender is intended to connect the ends of two different chains to create a chain of higher molecular weight. Chain extenders employ a variety of mechanisms to exploit a range of reaction conditions, product specifications and polymer chemistry. Four different types of chain extenders were used with PHB to determine which mechanism would be most effective with the biopolymer.

Chain extenders fall into one of two general categories, referred to here as activating-type chain extenders and addition-type chain extenders. Activating-type chain extenders are composed of an electrophilic site connected to suitably labile substituents. They act as intermediates for a substitution reaction linking the ends of two polymer chains, but ultimately do not become part of the extended chain. By contrast, addition-type chain extenders consist of at least two electrophilic sites and are intended to form a permanent bridge between at least two polymer chains.

Activating-type chain extenders are generally based either on a diester or diimide functionality. The first step in this class of chain extension is formation of a bond between the chain extender and a polymer carboxylate, resulting in a complex with increased electrophilicity on the polymer carboxylate carbon. The second step forms the extended polymer chain, by a substitution reaction in which an alcohol from another polymer attacks the carboxylate, ejecting the chain extender (Inata & Matsumura, 1985). The well-known DCC coupling reaction, shown in Figure 2.3 is an example of activating-type chain extension (Neises & Steglich, 1978).

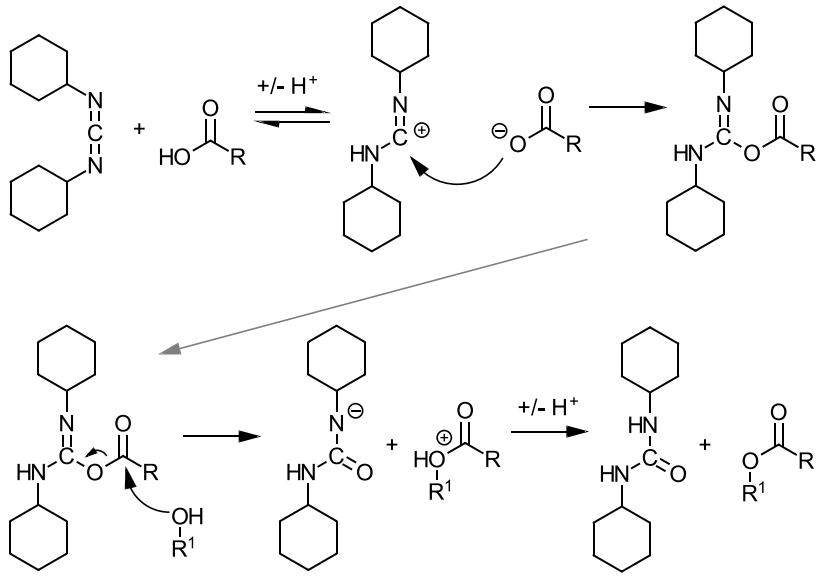

Figure 2.3: DCC reaction mechanism

Similarly, addition-type chain extenders are based on carbon electrophiles, except that the bond formed by addition is intended to be permanent. Electrophiles commonly include epoxides, isocyanates and anhydrides. In addition, heterocyclic molecules such as phenylene bisoxazoline have had success in coupling carboxylic acids and alcohols together from different chains (Inata & Matsumura, 1985) (Loontjens, et al., 1997). The latter reacts through a ring-opening reaction shown in Figure 2.4.

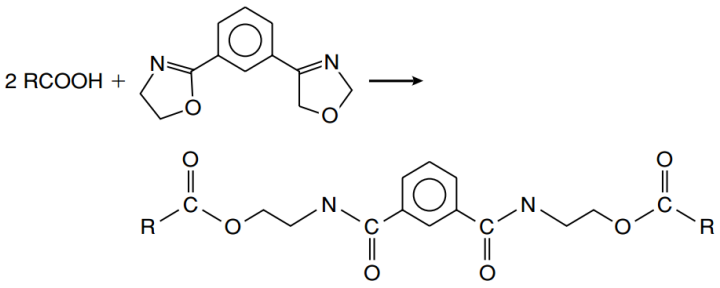

Figure 2.4: Ring-opening reaction of phenylene bis-oxazoline with two carboxylic acids, demonstrating the typical mechanism for chain extension of polyesters with bis-heterocycles. Reproduced from Loontjens et al. (Loontjens, et al., 1997)

For the present study of chain extender activity on PHBV, four chain extenders were acquired: an epoxy, an isocyanate, a heterocyclic dianhydride and a carbodiimide. Except for the carbodiimide, all the extenders are addition-type. The intended study was supposed also to include phenylene bisoxazoline, but the compound could not be acquired.

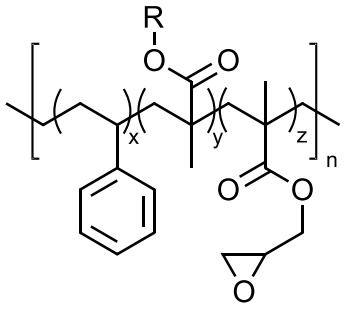

Figure 2.5: Structure of Joncryl - n, x, y, and z are not specified. Adapted from (Wang, et al., 2010)

The epoxide, Joncryl ADR 4368 (Figure 2.5), is a resin specifically designed for reaction with polyesters, and has been shown to significantly increase the molecular weight of PLA and PET (Wang, et al., 2010). Each Joncryl molecule has several epoxide functional groups, which are reasonably stable under normal conditions but will react quickly and irreversibly with carboxylates. Ultimately, several polymer chains should be bonded to each Joncryl molecule in a star or brush-shaped molecule (Villalobos, Awojulu, Greeley, Turco, & Deeter, 2006).

The second chain extender, hexamethylene diisocyanate, is a strong electrophile which converts to a urethane when attacked by alcohol through the reaction scheme shown in Figure 2.6 (Inata & Matsumura, 1985).

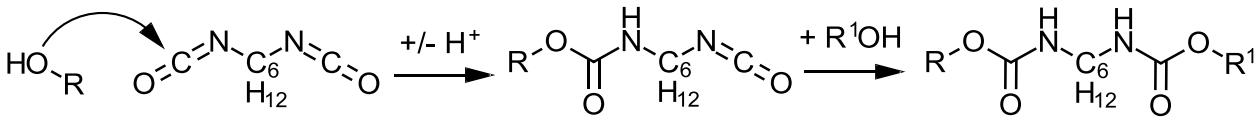

Figure 2.6: Chain extension mechanism for hexamethylene diisocyanate with polymers R and R^1 (Inata & Matsumura, 1985)

The third chain extender, pyromellitic dianhydride, is a heterocycle which reacts through a ring-opening substitution reaction at one of four carbonyl electrophiles. At moderate temperature, this yields the compound in Figure 2.7. However, it is possible for this compound to react further through Fischer esterification to convert the remaining carboxylic acids to esters, ultimately linking the molecule to four different polymer chains (Röhrsheid, 2012).

The fourth chain extender is the only activating-type extender selected. Polycarbodiimide operates through the coupling reaction already shown in Figure 2.3, yielding urea as byproduct. In the case of polyester chain extension, carbodiimides activate carboxylate end groups for

transesterification. No water is left as a byproduct of this reaction, a significant advantage for processing of polyesters.

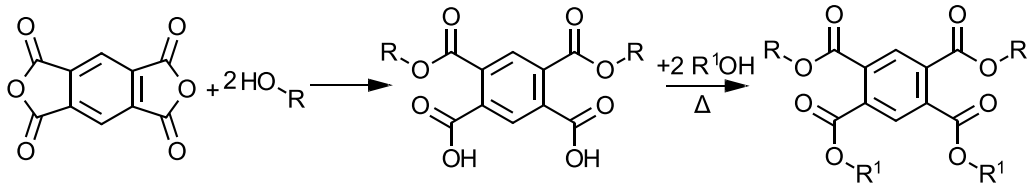

Figure 2.7: Chain extension mechanism for pyromellitic dianhydride to form a diester, and at elevated temperature to a tetraester (Inata & Matsumura, 1985)

These four chain extenders were selected based on two rationales: first, they all react readily with polyesters; and second, they represent a wide array of functionality to increase the likelihood that PHB will react favorably with at least one of the compounds chosen.

Chapter 3 Objectives

It should be clear from the preceding review that there is significant promise for PHB-based materials as a biodegradable polymer. Although the homopolymer is too brittle and thermally unstable to be used by itself in this capacity, promising results have been achieved with blended or copolymerized PHB systems. Although some improved PHB-based materials have been developed, none of these improvements have directly addressed the problem of thermomechanical degradation. Instead, degradation is avoided by reducing the melting temperature of the material. An effective remedy for thermomechanical degradation has yet to be found. Such a remedy is desirable even in PHB-based materials with depressed melting points, because it would allow these materials to be blended with other polymers having high processing temperatures.

Chain extension was identified as a method to address degradation in PHB, based on the reported effectiveness of chain extenders in increasing average molecular weight of a range of polyesters. Because the chemical structure of PHB is similar to PLA, and to a lesser extent PET, it was presumed that chain extenders which reacted with the latter two polymers would also react effectively with PHB.

3.1 General Objectives

1. To develop a PHB-based material whose molecular weight remains stable during processing at temperatures where it is subject to thermomechanical degradation.
2. To blend PHB with PLA to form a thermally stable, biodegradable blend, and to determine the effect of chain extension on the PHB-PLA blend

3.2 Specific Objectives

1. To characterize the effect of processing on PHB
2. To find a chain extender with suitable functionality to stabilize PHB during compounding at 180^{o}C.
3. To produce blends of PHB and PLA at weight ratios of 75% PHB/25% PLA, 50% PHB/50% PLA and 25% PHB/75% PLA, and to observe the effect of adding a chain extender to these blends on chemical stability, on tensile properties and on morphology.

Chapter 4 Experimental

The experiment was intended to occur in several stages, beginning from characterization of the polymer, followed by determination of the best chain extender and ending with characterization of the PHB-PLA blend.

4.1 Materials

PLA 4032D was supplied in the form of pellets by NatureWorks LLC., of Blair, Nebraska, containing 1.5% D Isomer, 0.19% residual lactide and having a relative viscosity of 3.98. PHBV Enmat Y1000P was supplied as pellets by Tianan Biologic Material Co. Ltd., of Ningbo, China; according to the supplier, the polymer contained 2% valerate, had an average molecular weight between 200kDa and 250kDa, a melt index between 6.0 and 10.0 grams per 10 minutes at 190^{o}C under 2.16kg, a specific gravity of 1.25, and contained an unspecified antioxidant and nucleating agent

Joncryl® ADR 4368-C was supplied by BASF in the form of a white powder; according to the supplier the polymer had an epoxy equivalent weight of 284 grams per mole and an average molecular weight of 6502 Da. Polycarbodiimide and pyromellitic dianhydride were all supplied by Sigma-Aldrich as white powders, while hexamethylene diisocyanate was supplied as a liquid from the same supplier.

4.2 Challenges of Bulk-Phase Reactions

As is the case in most fields of research, the conditions most conducive to study of polymer chemistry differ greatly from the conditions typical of the industrial processes where this research usually finds its application. Generally, industrial processes are performed on the undiluted molten polymer, referred to as the ‘bulk’ phase. Mixing additives into the bulk phase is complicated by the fact that the polymer is very viscous while having very low diffusivity – in order to produce anything resembling a homogeneous mixture, a great deal of shear must be applied to the polymer. The slow diffusivity of the molten polymer means that, if handled poorly, fast-acting reagents such as peroxides might react completely at the polymer-additive interface without ever being exposed to the bulk of the polymer. Further complicating the picture, the shear required to mix the polymer generates heat due to viscous dissipation. In the

case of PHB, where the temperature dictates the rate of degradation, this last phenomenon is understandably problematic

For the purposes of scientific study, it is preferable that a reaction occur in a controlled environment where important parameters such as the reaction rate and the stoichiometry can be quantified with accuracy. This can be accomplished by performing the reaction in solution. By diluting the polymer, the limiting effects of mass transfer which prove so troublesome in the bulk phase are eliminated. Further, the solution provides a heat sink for the reaction which allows the temperature to be controlled to a greater extent. Because the medium can be controlled more precisely, significant results can be achieved with smaller quantities of polymer and reagent, and the products can be characterized more accurately.

Of course, solution-based reactions do not accurately reflect the realities of bulk-phase polymer processing. This is demonstrated in the work of Hong et al. in their article on grafting maleic anhydride to PHBV, in which the results of melt-grafting, solution-grafting and mechanical grafting were compared (Hong, Lin, & Lin, 2008). The amount of degradation and the quality of the graft are incomparably different depending on the method of preparation.

As noted elsewhere in this work, a solvent could not be found for the grade of PHB used for these experiments. This was problematic for two reasons. First, the effectiveness of reaction with chain extenders could not be tested in a more controlled environment, and second, it required experiments be performed in conditions where PHB degradation was inevitable.

When preparing an experimental protocol for compounding, the issue of degradation was considered paramount. Consequently, the set temperature for compounding was as close to the PHB melting point as possible, at 175^{o}C. Tests at lower temperatures (172.5^{o}C and 170^{o}C) took significantly longer to melt the polymer, and concerns were raised about the quality of mixing. Mixing time and rotor speed were set at 10 minutes and 60 rpm, higher than absolutely necessary for PHB, a decision that was made to ensure beyond any doubt that the polymer was well mixed with the additive.

4.3 FTIR for Bulk-Phase Chemical Analysis

Despite the lack of solubility of the grade of PHB used in these experiments, rudimentary chemical analysis is still possible through the use of FTIR. The importance of this analytical tool is reflected in the fact that the IR spectrum of PHB is easily found on the internet. The significant peaks in this spectrum are shown in Table 4.1 below. This spectrum was used in attempts to characterize degradation and chain extension reactions. Use of FTIR is discussed further in the results section as well as Appendix 3.

Table 4.1: PHB IR peaks

Vibrational Mode	Wavenumber (cm-1)
C-O stretch	1050, 1096, 1128, 1180
C-O-C stretch, crystalline	1128, 1263, 1278, 1289
C-O-C stretch, crystalline	1259, 1302
CH3 symmetric deformation	1378
CH3 asymmetric deformation	1449
CH2 deformation	1458
C=O stretch, crystalline	1723
C=O stretch, amorphous	1740
CH2, CH3, symmetric stretch	2875
CH2 asymmetric stretch	2933
CH3 asymmetric stretch, crystalline	2967
CH3 asymmetric stretch, crystalline	2974
CH3 asymmetric stretch, amorphous	2983
CH3 asymmetric stretch, crystalline	2995
CH3 asymmetric stretch, crystalline	3009
C=O overtone, crystalline	3436

4.4 Stage 1: Sample Characterization

In this stage, the basic elements of protocol were established. In experiments which have not been presented, the effect of moisture on the polymer was determined. The moisture content of the polymer was required to be less than 250ppm by the manufacturer. This condition was tested by Karl-Fischer titration, with three repetitions performed for each sample. Ultimately, this resulted in the decision to dry the polymer before any step that required melting the polymer: before processing, polymers were dried at 60^{o}C for 12h. Pellets were dried in an industrial dryer at atmospheric pressure, while regrind and samples were dried under vacuum in in lab ovens at 60^{o}C.

Table 4.2: Moisture content of PHB samples, determined by Karl-Fischer titration

Sample	Mass (g)	Moisture Content (ppm)
Undried Virgin PHB Pellet	0.374	629
Pellets dried for 12 hours	0.510	25
Pellets dried for 84 hours	0.489	24
Undried Compounded PHB	0.304	371
Compounded PHB dried for 12 hours	0.414	22

Compounding was performed in a Haake internal mixer with Banbury type rotors and a chamber volume of 310 mL. The polymer was compounded at a setpoint temperature of 1750C and a rotor speed of 60RPM for 10 minutes, after which it was air cooled to room temperature then ground into irregular pellets (referred to as regrind) using a grinder with a 0.5 mm screen. Chain extenders were added to the polymer during compounding, two minutes after the occurrence of peak torque.

The technique of Melik and Schechtman (Melik & Schechtman, 1995), mentioned previously in this work, was used to establish the extent of degradation during compounding. This method was supplemented by parallel-plate rheometry of samples compounded for a range of residence times.

Samples for rheometry compression-moulded from regrind by first heating samples to 1800C at a pressure of 0.8MPa, then compressing samples to 10MPa at 1800C for five minutes, followed by cooling to room temperature under a constant pressure of 10MPa. Rheometry samples were discs with a diameter of 25mm and a thickness of between 1.4 and 1.8mm.

Complex viscosity was determined by parallel-plate rheometry using an MCR301 rheometer. The rheometer was preheated to 180^{o}C before samples were loaded. Once a sample was loaded into the rheometer, the sample was allowed 4 minutes to heat to testing temperature. During preheat, the sample was gradually compressed to a thickness of one millimeter, and trimmed of excess material. After preheating, an oscillating shear was applied for 600 seconds, at a shear strain amplitude of 5% and a frequency of 0.1 radians per second. Complex viscosity was recorded every 15 seconds. In order to verify measurements, at least three repetitions were performed.

4.5 Stage 2: Chain Extension

In this stage, the four chain extenders were added to the compounder at three different concentrations, with specific concentrations determined by practical considerations like the density of the chain extender and the quantity of the extender available. The initial objective was simply to produce a measurable change. The amounts can be seen in Table 4.3. The quality of chain extension was evaluated based on the complex viscosity change of the polymer.

Table 4.3: Concentration of chain extenders in PHB samples

Chain Extender	Low Concentration (% wt)	Mid Concentration (% wt)	High Concentration (% wt)
Joncryl	0.5%	1%	2%
Hexamethylene Diisocyanate (HMDI)	0.25%	0.5%	1%
Pyromellitic Dianhydride (PMDA)	0.5%	1%	2%
Polycarbodiimide (PCDI)	0.5%	1%	2%

4.6 Stage 3: Blending with PLA

In this stage, PHB and PLA were compounded by themselves as well as in blends in three ratios, (75% PHB/25% PLA, 50% PHB/50% PLA and 25% PHB/75% PLA) for a total of five different compositions. Each sample was also compounded with the most effective chain extender. As with the previous section, the initial goal was not to optimize the chain extender but rather to produce a noticeable change in properties.

The tensile properties of the samples were then determined and compared to morphology in order to determine whether any synergistic properties had been produced by blending. Samples were annealed prior to tensile testing to eliminate the aging effects caused by secondary crystallization. Annealing conditions were taken from Kurusu et al.: 1000 minutes at 120^{o}C (Kurusu, Demarquette, Gauthier, & Chenal, 2012).

Tensile testing was performed on an Instron tensile testing machine with a 5kN load cell. An extensometer was attached to samples during testing to more accurately plot strain. During testing, the strain rate was controlled at 1 mm per minute. At least 10 repetitions were performed for every sample to ensure consistency. Samples for tensile testing were compression-moulded to conform to the standards of ASTM D638-10, specifically the type V sample, using the same processing conditions outlined in the description of rheological sample preparation.

Chapter 5 Results

5.1 Degradation and Chain Extension of PHB

5.1.1 Compounding

Torque and temperature were plotted during compounding, which permitted the effect of degradation to be monitored in real time. The effect of chain extenders on the polymer can be seen from Figure 5.1, comparing the torque required to compound neat PHB with the torque required to compound PHB with 1% and 4% Joncryl by weight. At approximately 150 seconds, the addition of the chain extender can be identified by a sudden drop in torque encountered when the mixing chamber is opened. After this event, a gradual upwards deviation in torque is observed relative to the torque curve of neat PHB, indicating increased viscosity. This deviation of the melt suggests Joncryl reacted with PHB resulting in increased molecular weight.

Figure 5.2 shows PHB compounding torque plotted logarithmically as a function of temperature, in order to perform the analysis of Melik and Schechtman already outlined elsewhere in this document (Equation 2.5). Only a small segment of the curve is linear, due to increased viscosity during melting as well as decreased viscosity as a result of degradation. The slope of the linear region was used to develop a prediction of torque for a completely molten, non-degrading polymer. This prediction is compared to an actual torque curve in Figure 5.3 with the conclusion that degradation occurs early in the compounding session.

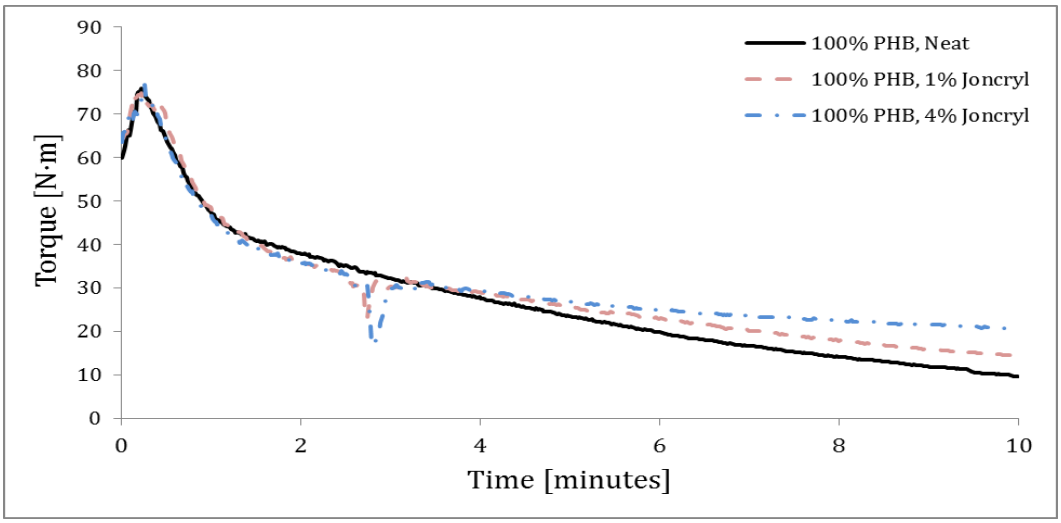

Figure 5.1: Torque curve of PHB, showing the effect of Joncryl

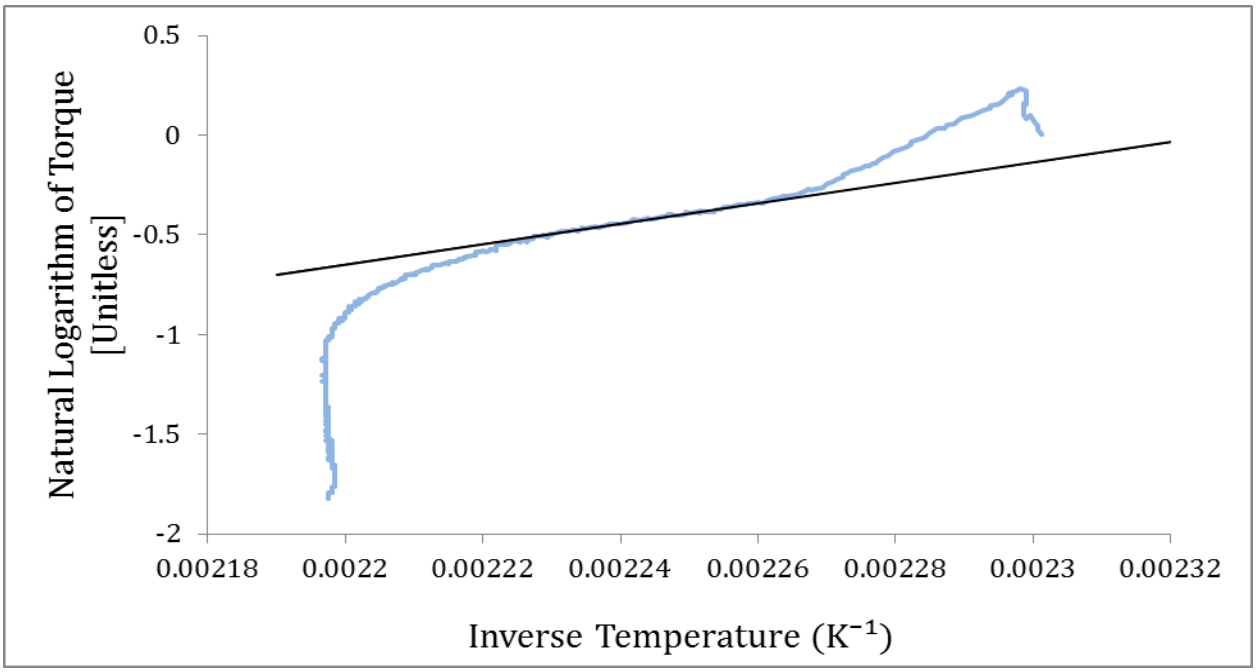

Figure 5.2: PHB compounding torque curve plotted as a function of inverse temperature (blue). The torque curve of an inert liquid polymer should plot a straight line. A trend line (black) has been added to highlight the region where PHB was completely molten and degrading relatively slowly

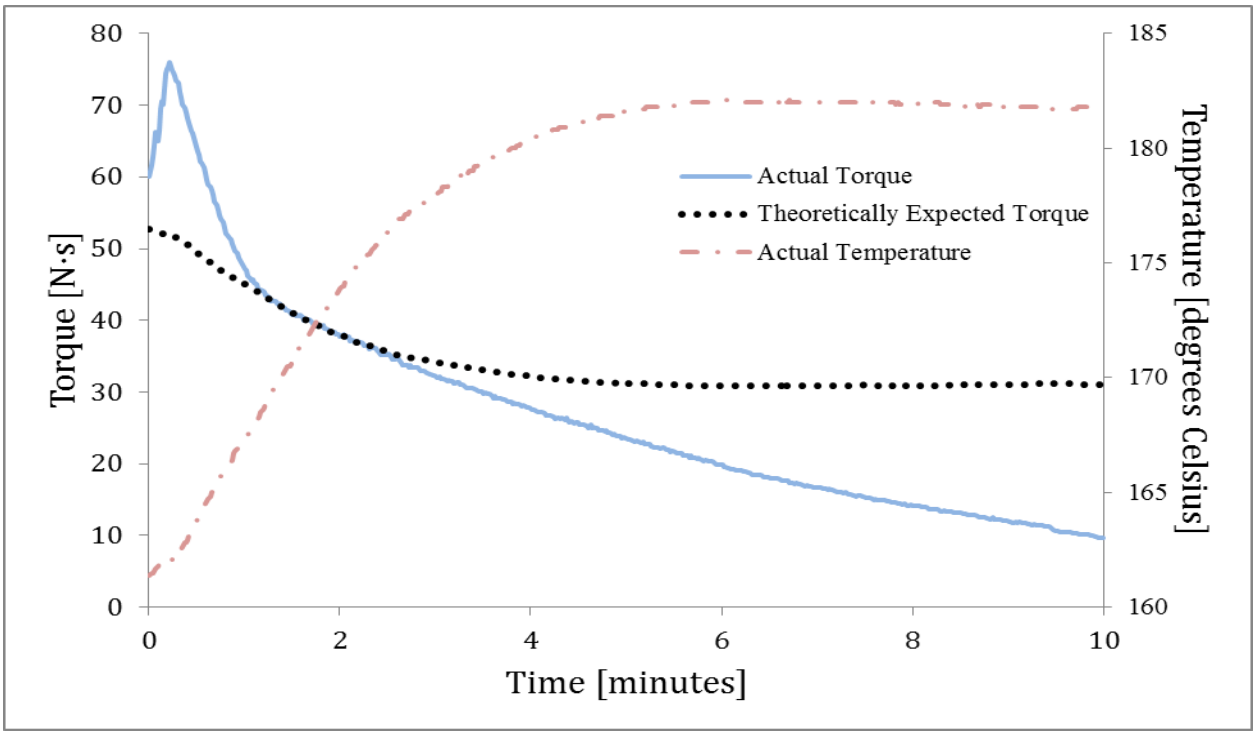

Figure 5.3: Torque curve from Figure 9 (blue), plotted on a graph of torque as a function of time, with mixing chamber temperature (red) and predicted torque of an inert molten polymer at the same temperature (black)

5.1.2 PHB Degradation Characterized via Rheology

Changes in molecular weight of samples were inferred from complex viscosity through rheology. Figure 5.4 shows the effect of compounding on PHB molecular weight. The sample which was not exposed to compounding has a much higher complex viscosity than a sample of PHB after 10 minutes compounding. The change between the complex viscosity of PHB after 30 minutes is only slightly less than it was after 10 minutes, suggesting that the majority of degradation occurred in the first ten minutes of compounding. Complex viscosity decay followed the same exponential trend for all three samples.

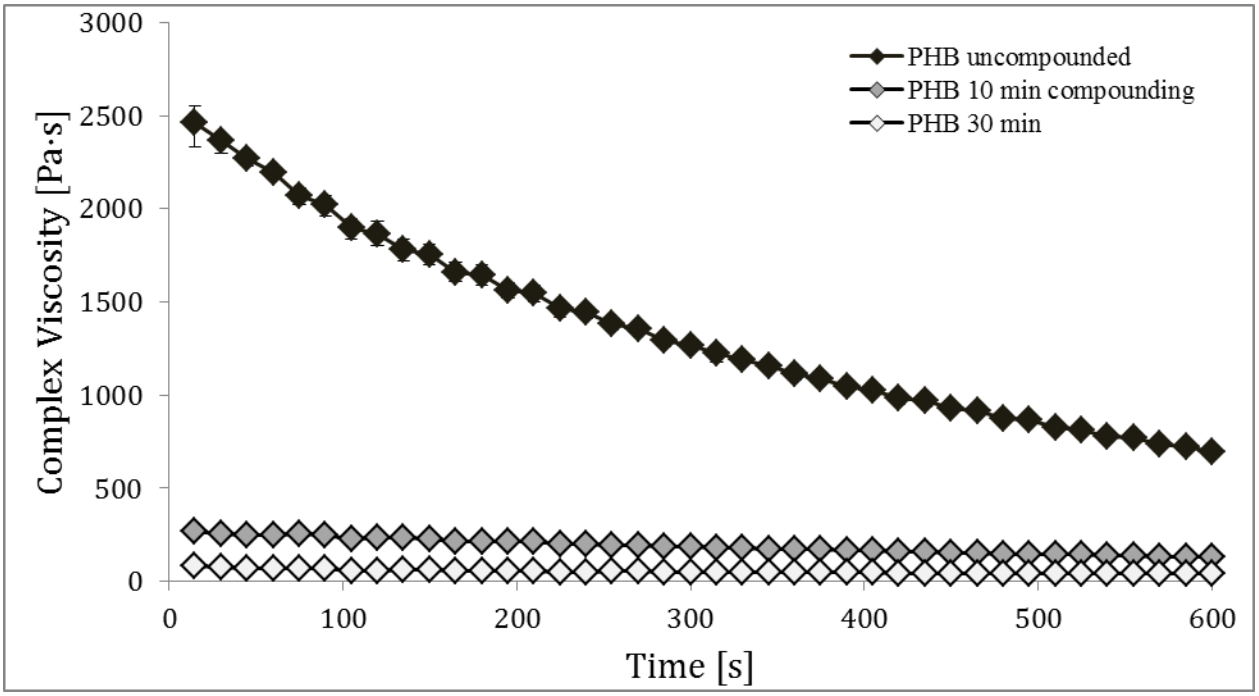

Figure 5.4: Effect of compounding on PHB complex viscosity

5.1.3 PHB Degradation Characterized via FTIR

In order to determine if degradation could be detected in FTIR, a comparison was made between the spectra of PHB pellets and PHB which had been compounded for 10 minutes. Spectra were normalized so that the ester carboxyl stretch at approximately 1720 cm-1 was equal to four arbitrary units of intensity. This was based on the assumption that differences in individual spectrum intensity did not reflect actual differences in concentration but rather effects characteristic of the FTIR apparatus which resulted in some samples returning a stronger signal than others.

The first test of degradation was to see if a difference existed between the spectrum of PHB pellets and that of PHB compounded for 10 minutes. In Figure 5.5, Figure 5.6 and Figure 5.7 three different samples of PHB compounded for 10 minutes are compared to the pellets. The variation between the three compounded samples is greater than the variation between any of the samples and the pellets, suggesting that the difference in absorption between the pellets and the compounded polymer is essentially irrelevant. As discussed in Appendix A3, an earlier attempt had been made to characterize degradation via FTIR, but this attempt proved inconclusive.

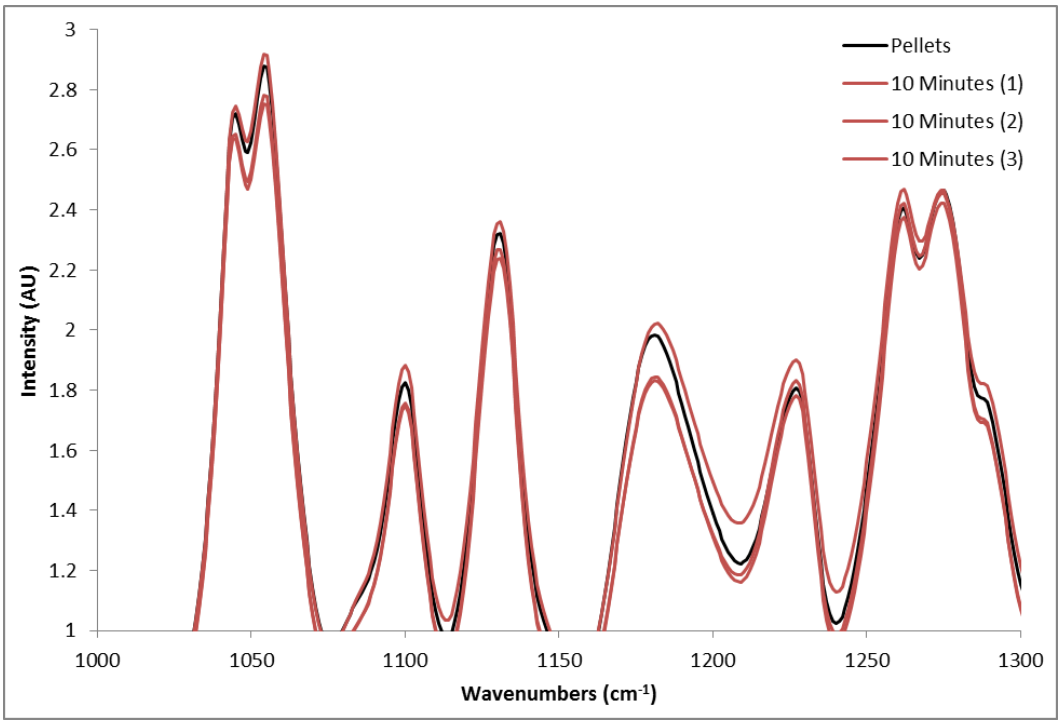

Figure 5.5: Ether and ester C-O stretch region of IR spectrum, showing PHB pellet (black) and three samples PHB compounded for 10 minutes (red)

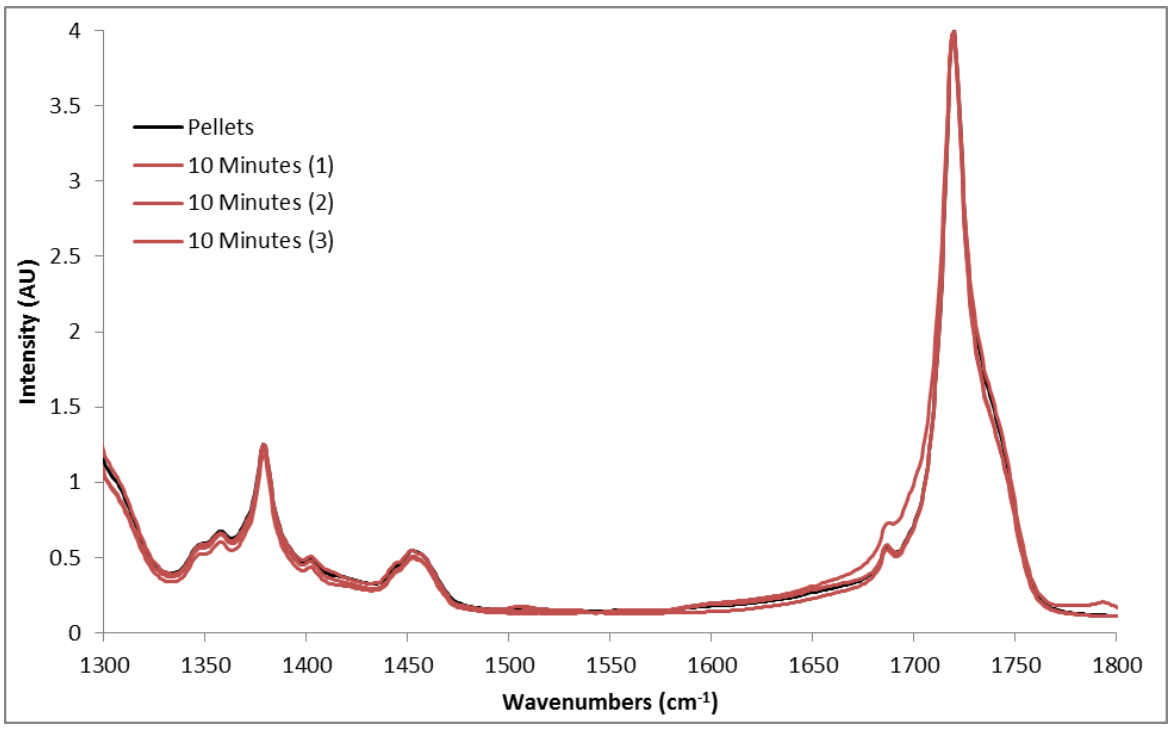

Figure 5.6: C-H bend and C=O stretch region of IR spectrum, showing PHB pellet (black) and three samples PHB compounded for 10 minutes (red)

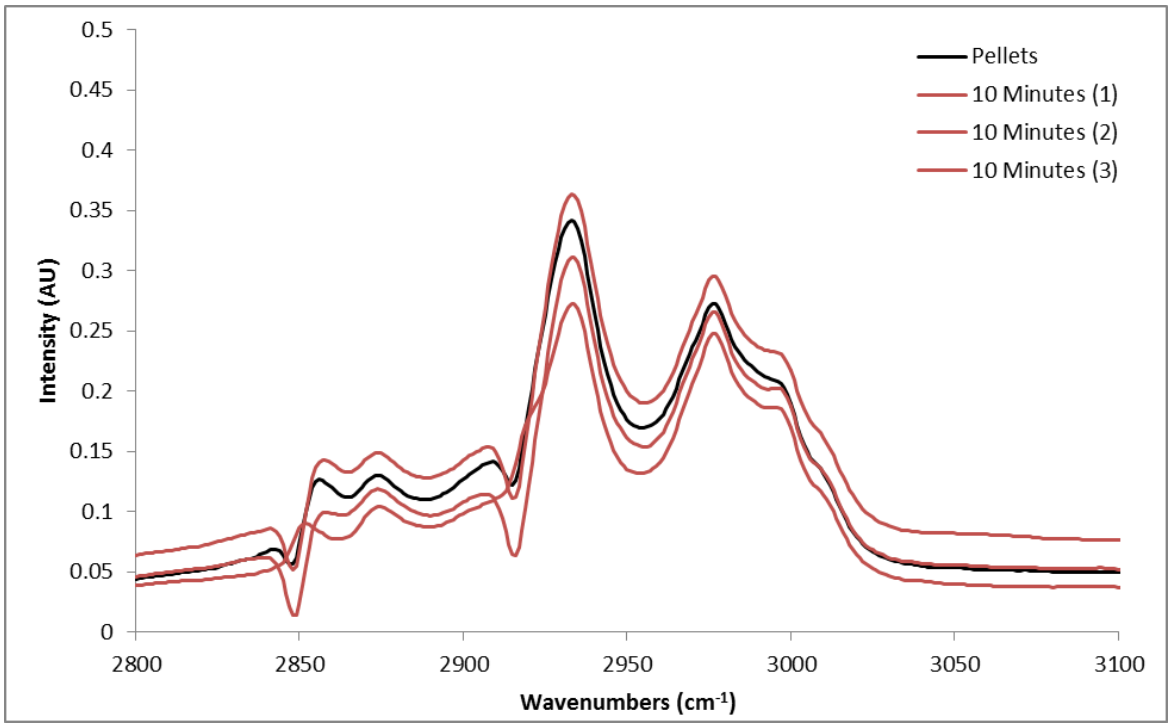

Figure 5.7: C-H stretch region of IR spectrum, showing PHB pellet (black) and three samples PHB compounded for 10 minutes (red)

5.1.4 Rheology of Chain Extended PHB

Four different chain extenders were added to PHB. The effect of their addition on PHB complex viscosity as a function of time is shown in Figure 5.8-5.11. Pyromellitic dianhydride and polycarbodiimide do not appear to yield any increase in complex viscosity, while addition of hexamethylene diisocyanate results in a slight increase, and Joncryl substantially increases the polymers' complex viscosity. The effect of all four chain extenders are compared in Figure 5.12. Significantly, none of the chain extenders alters the rate of degradation, although some effect on complex viscosity is apparent. From this information it is inferred that the successful chain extenders reacted to completion during compounding but their action did not inhibit future degradation.

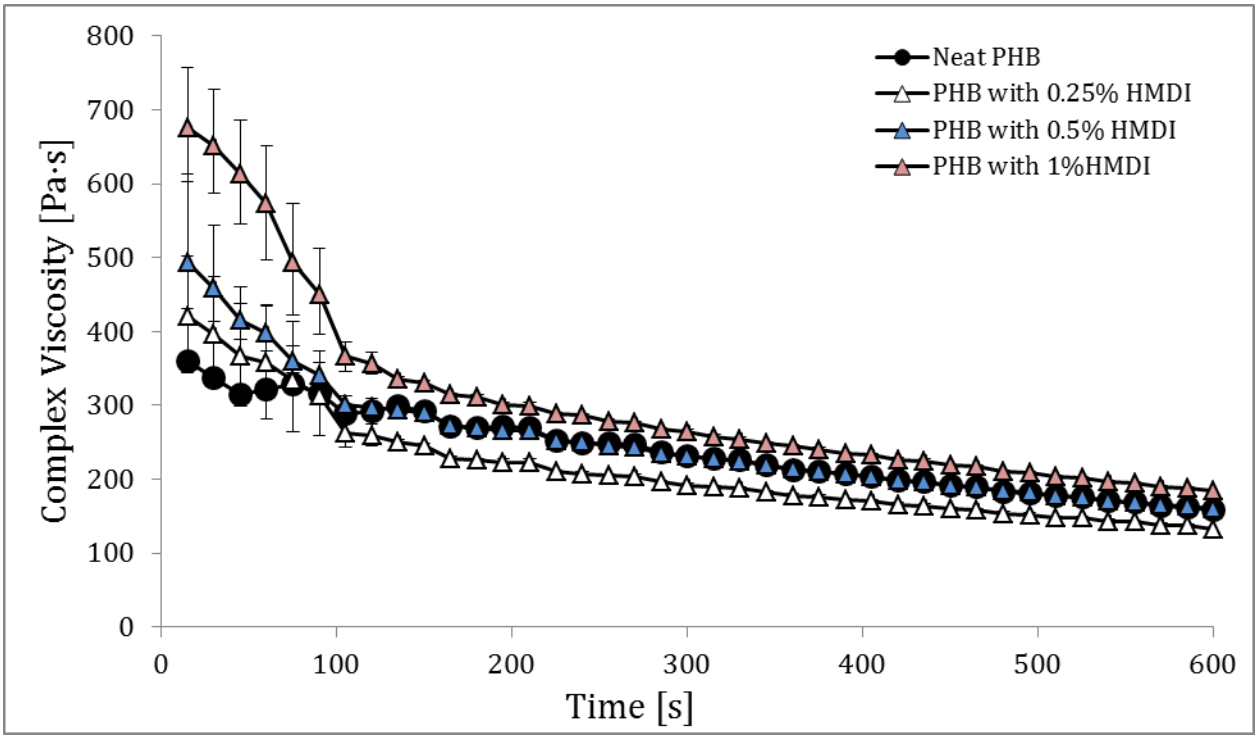

Figure 5.8: Complex viscosity of PHB, neat and with HMDI

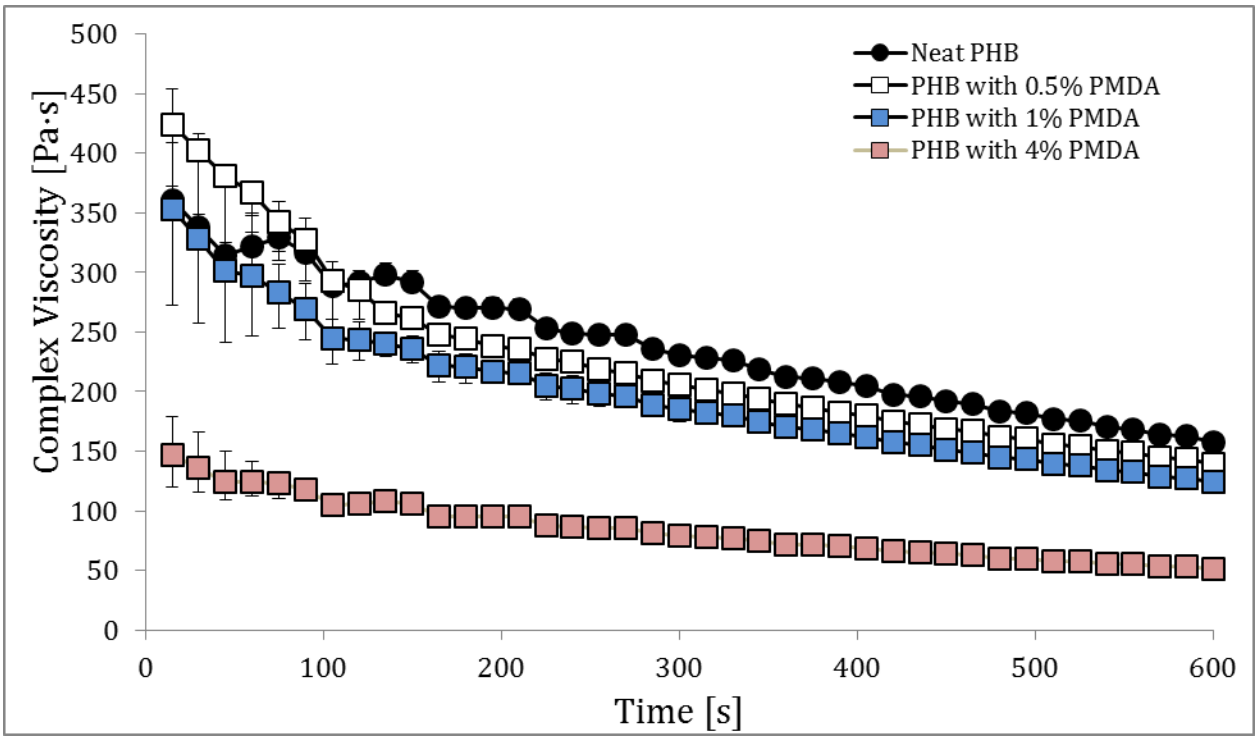

Figure 5.9: Complex viscosity of PHB, neat and with PMDA

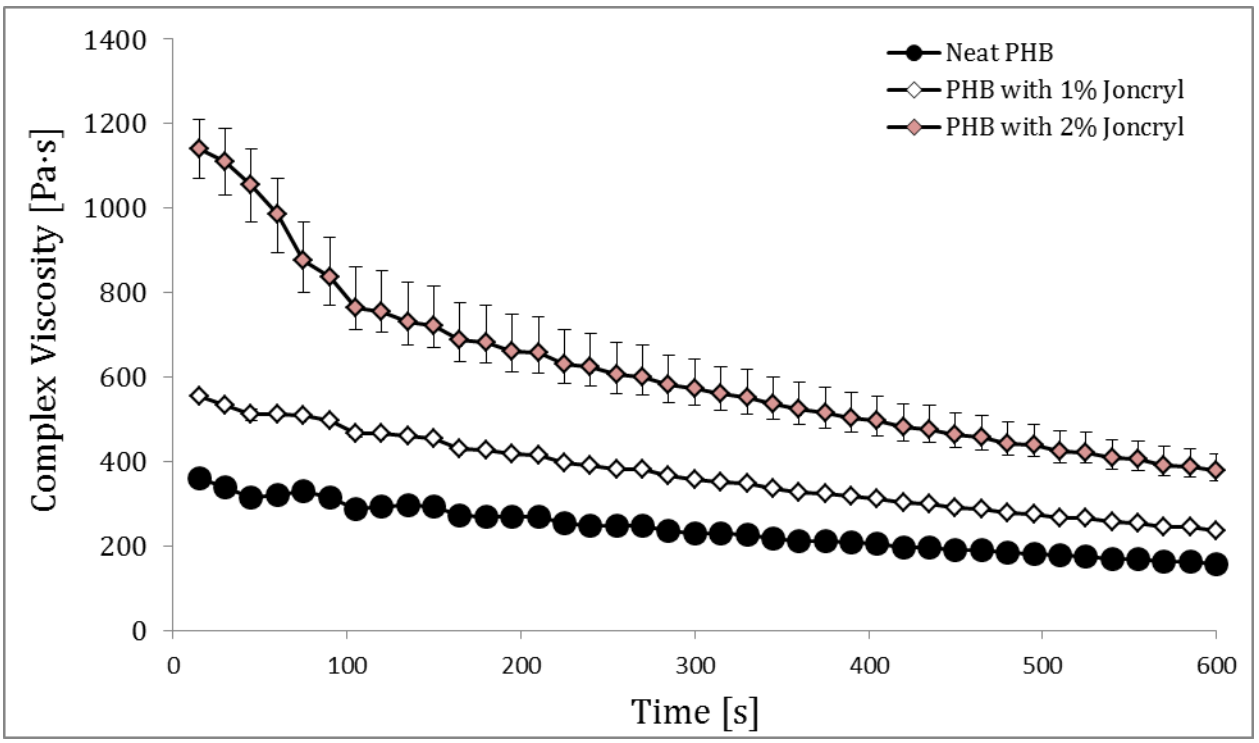

Figure 5.10: Complex viscosity of PHB, neat and with Joncryl

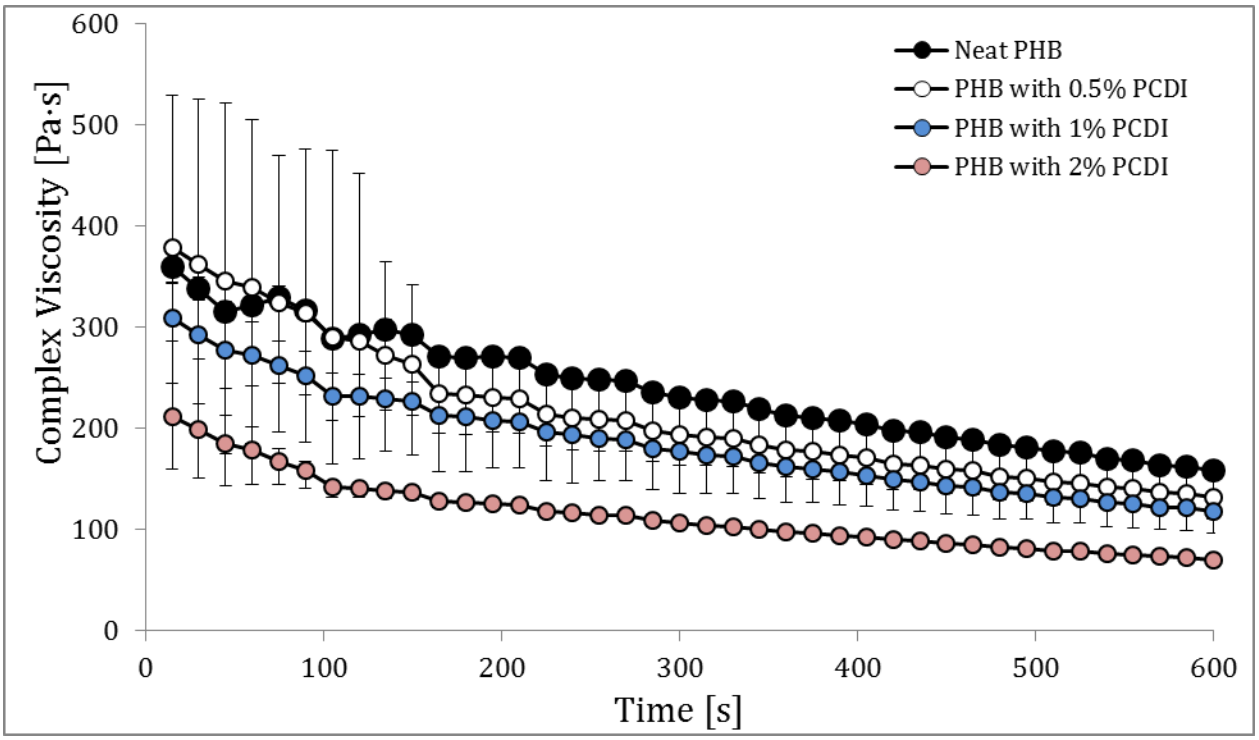

Figure 5.11: Complex viscosity of PHB, Neat and with PCDI

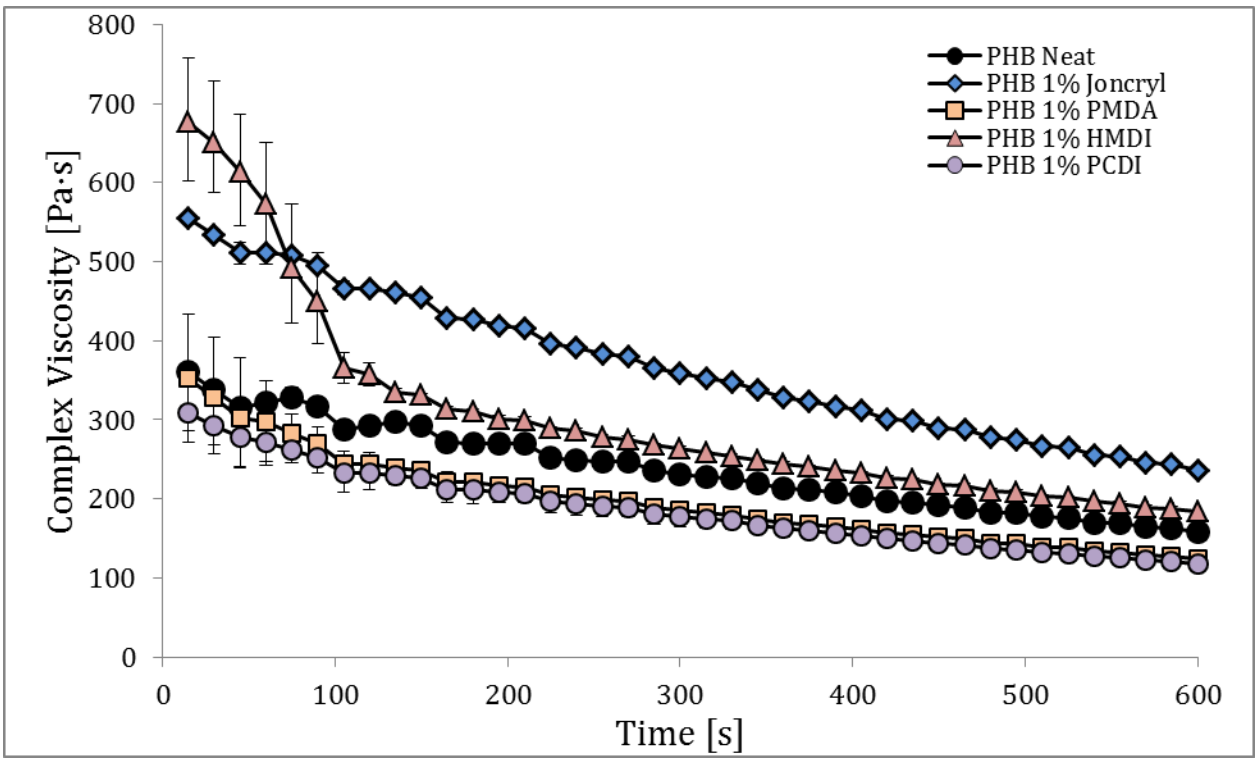

Figure 5.12: Complex viscosity decay of neat PHB compared to PHB with 1% of each chain extender

5.1.5 FTIR Analysis of Chain Extension

The IR spectra of chain-extended PHB samples, shown in Figure 5.13-16, were compared in order to determine if any change in the spectrum could be correlated to changes in complex viscosity, using the protocol outlined in the analysis of degradation. The spectra of Joncryl-loaded and PMDA-loaded PHB samples do not differ significantly from that of neat PHB, although some indication of a chemical reaction is suggested in the spectrum of HMDI. The possibility of a chemical reaction in the HMDI-loaded sample is based on the general offset of these reactions to higher intensity, and because of the change of shape at 2850 cm-1. However, the C-O stretch region remains unchanged. Further, no N-H or amido acyl stretch bands are visible, suggesting that the isocyanate was not concentrated enough to be visible. The PCDI spectra have some small variations from PHB samples, in the C-O stretches at 1180, 1228, 1260 and 1274 cm-1, as well as a small peak at 1804 suggesting the presence of an acyl stretch from the urea produced by consumption of isocyanates.

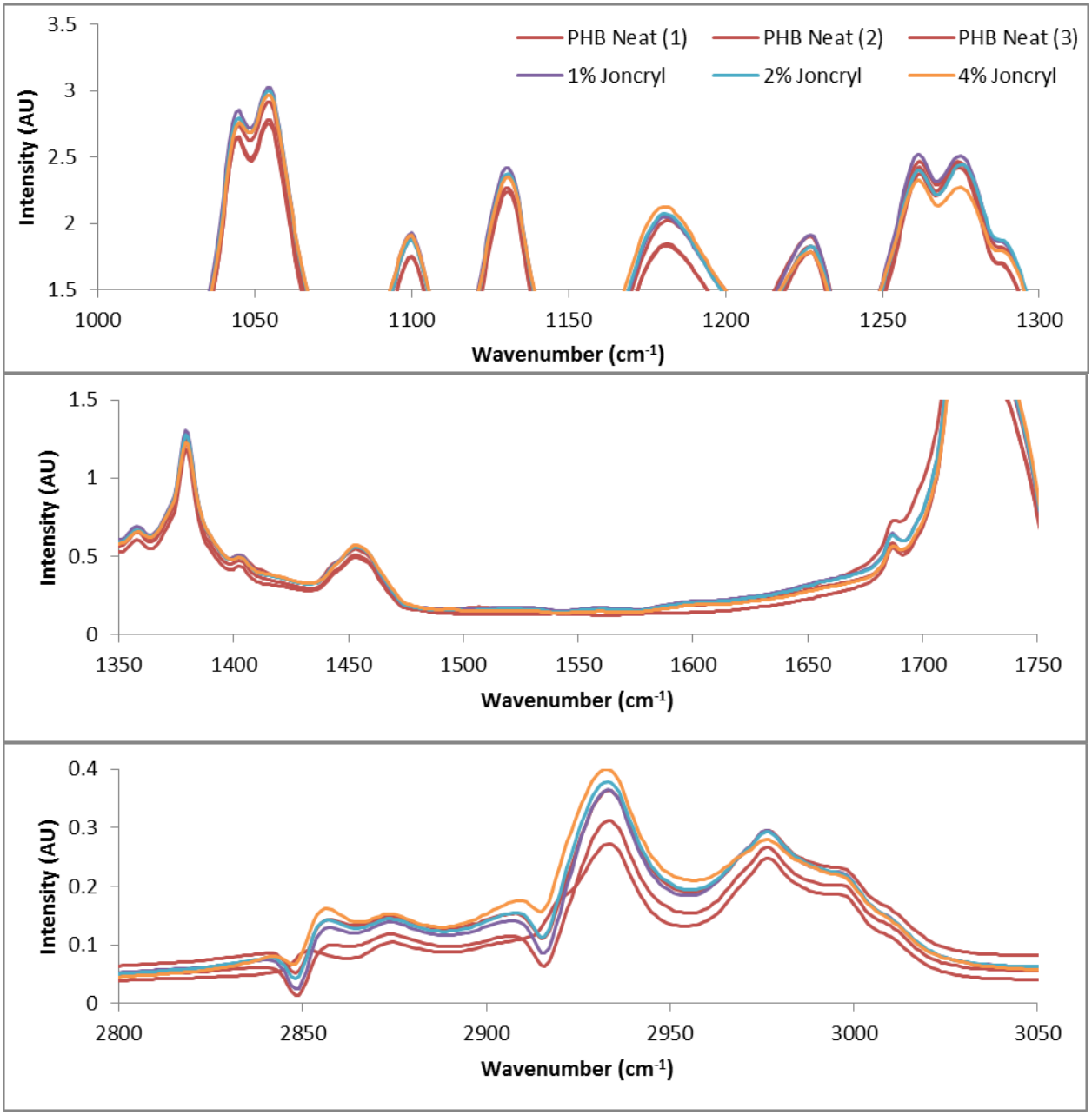

Figure 5.13: Normalized spectra of three samples of neat PHB compared to normalized spectra of PHB compounded with Joncryl

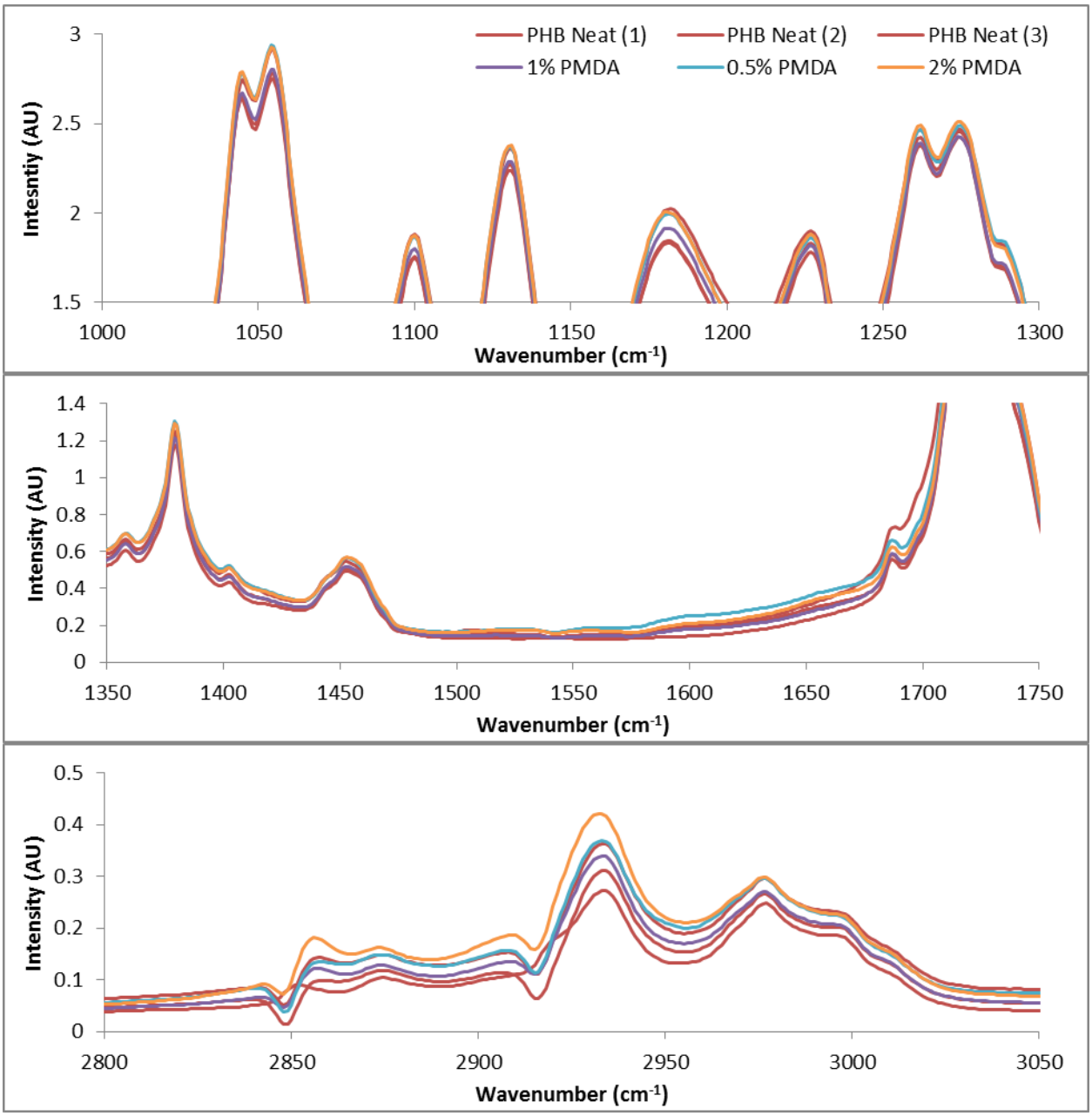

Figure 5.14: Normalized spectra of three samples of neat PHB compared to normalized spectra of PHB compounded with PMDA

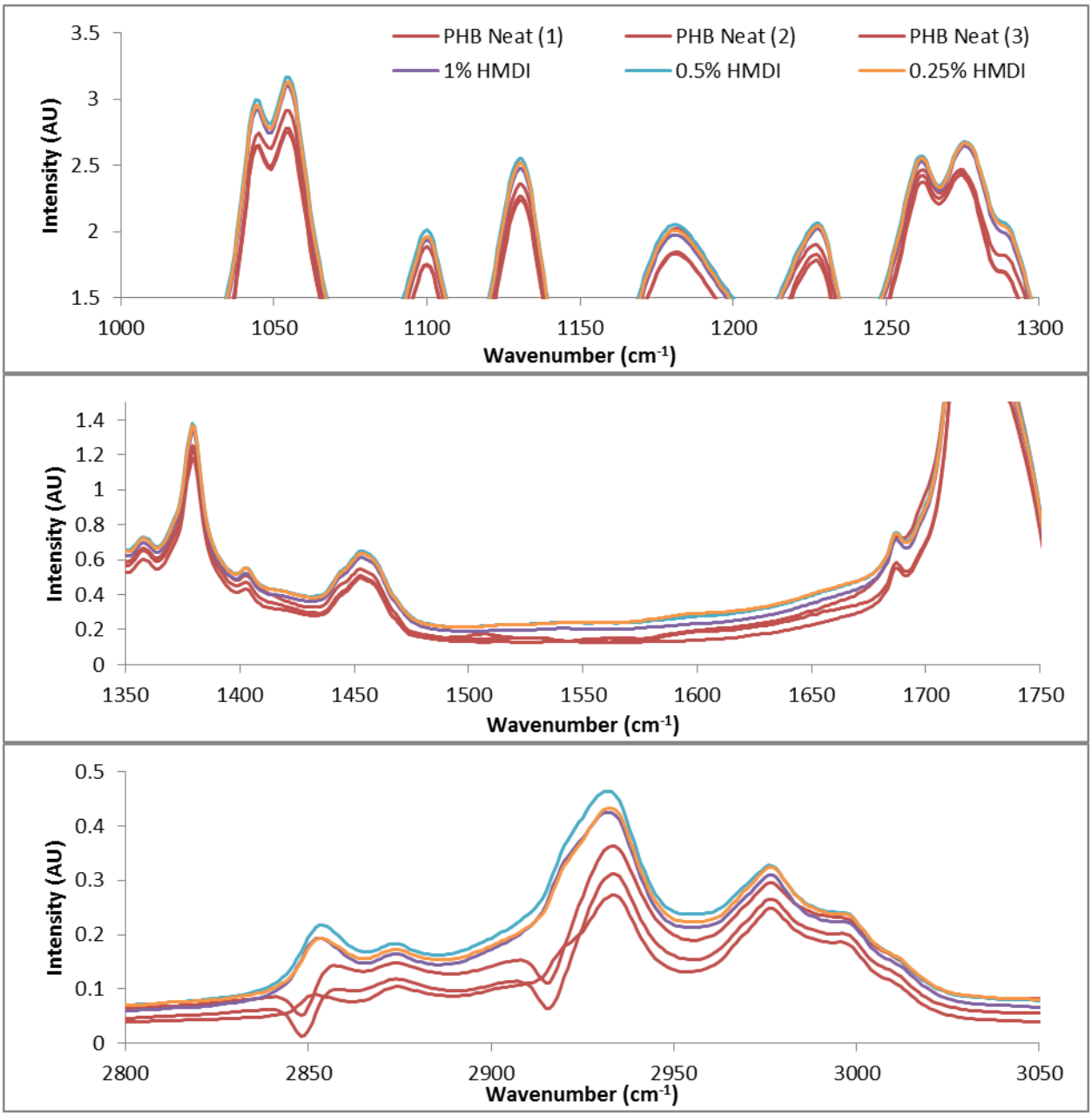

Figure 5.15: Normalized spectra of three samples of neat PHB compared to normalized spectra of PHB compounded with HMDI

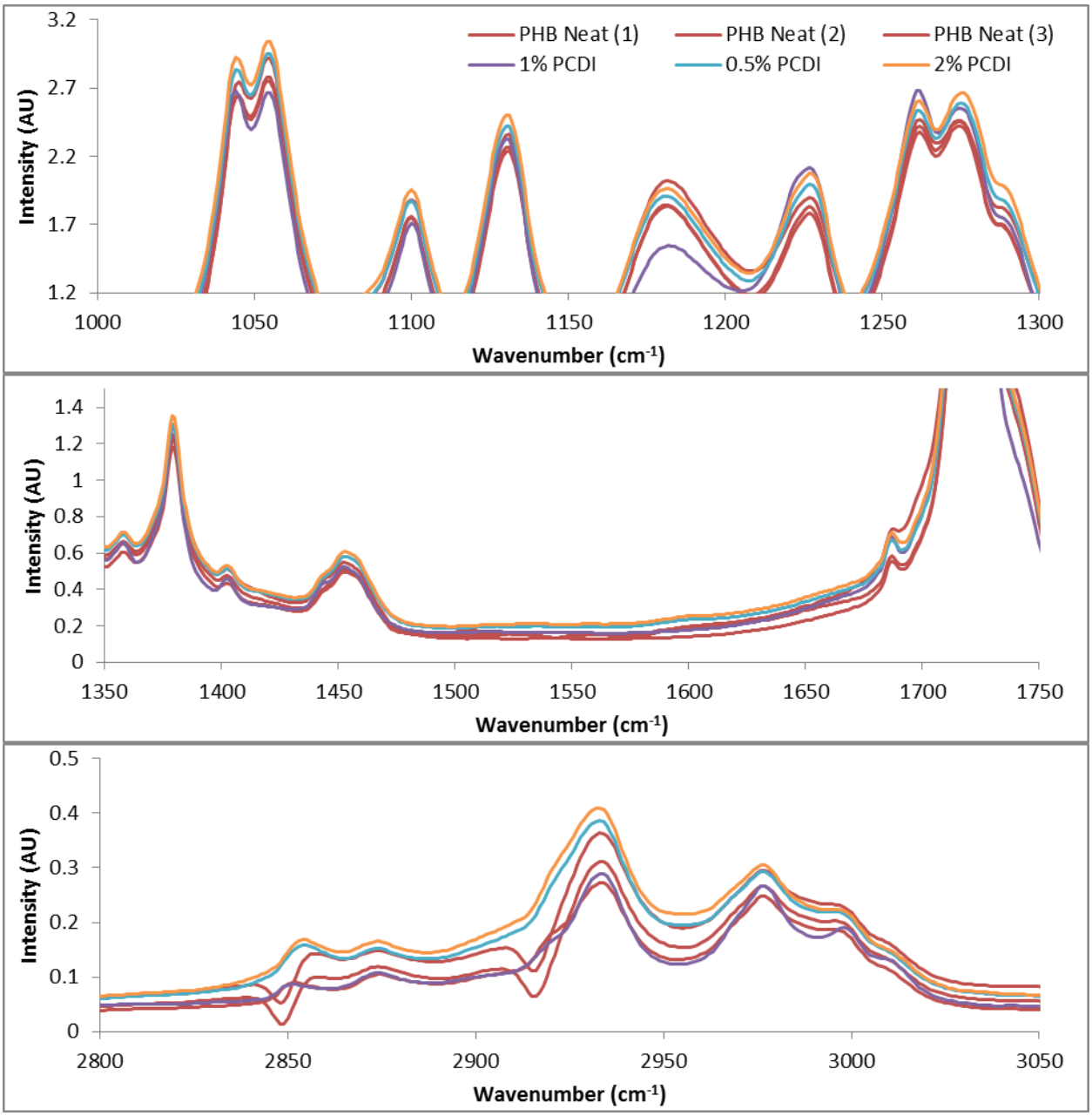

Figure 5.16: Normalized spectra of three samples of neat PHB compared to normalized spectra of PHB compounded with PCDI

5.2 PHB-PLA Blend Rheology and Mechanical Properties

5.2.1 Blend Rheology

The complex viscosity of PHB-PLA blends are shown in Figure 5.17. Blends in which PLA was the major component had significantly greater complex viscosity than blends in which PHB was the major compoent. The 75% PLA/ 25% PHB blend has approximately the same complex viscosity as 100% PLA, while the 25% PLA/75% PHB blend and the 50% PLA/50% PHB had progressively higher complex viscosity than 100% PHB despite having the same continuous phase. This suggests that droplets of PHB do not significantly alter the viscosity of the PLA matrix, while PLA droplets augment the PHB matrix viscosity. The effect of addition of Joncryl can be seen in Figure 5.18 and Figure 5.19. Joncryl increased complex viscosity, with larger increases experienced by polymers with a greater proportion of PLA in the blend. PLA and the 25% PHB/75% PLA blend experienced such a large increase in complex viscosity that a separate graph was needed to display the data. In addition, the complex viscosity of the 50% PHB/50% PLA blend and the pure PLA blend continue to rise during the experiment, suggesting that the reaction between Joncryl and the polymer has not completed.

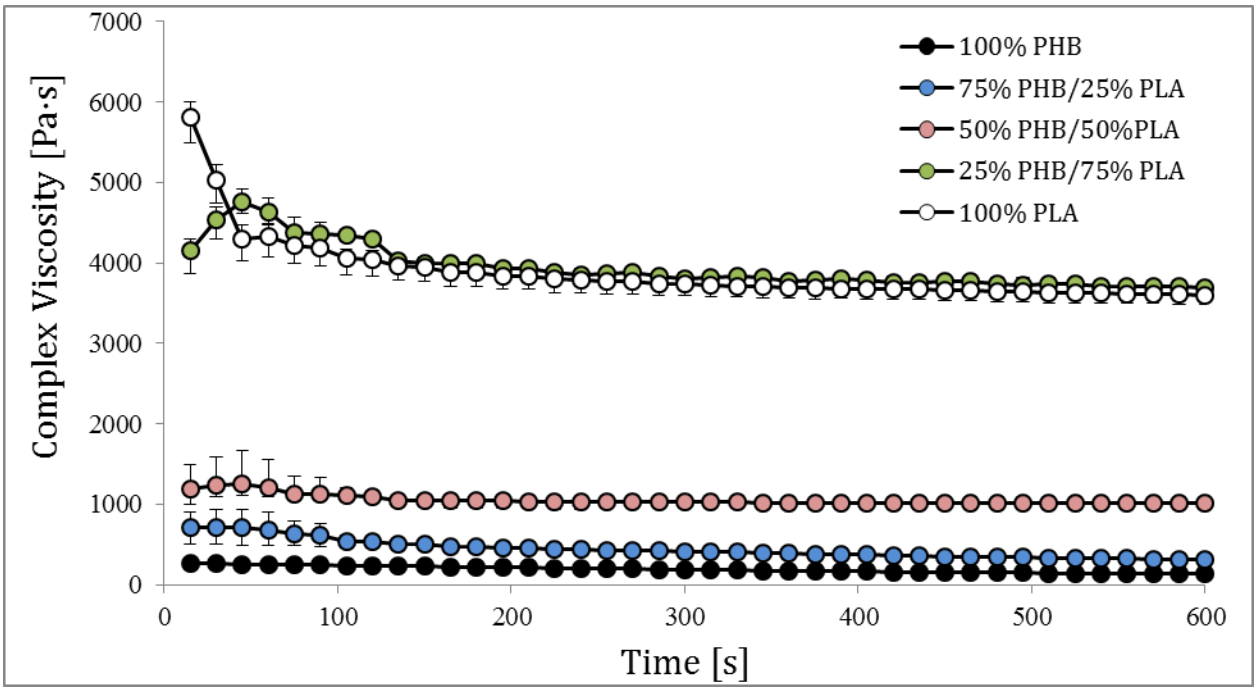

Figure 5.17: Complex viscosity of neat PHB/PLA blends

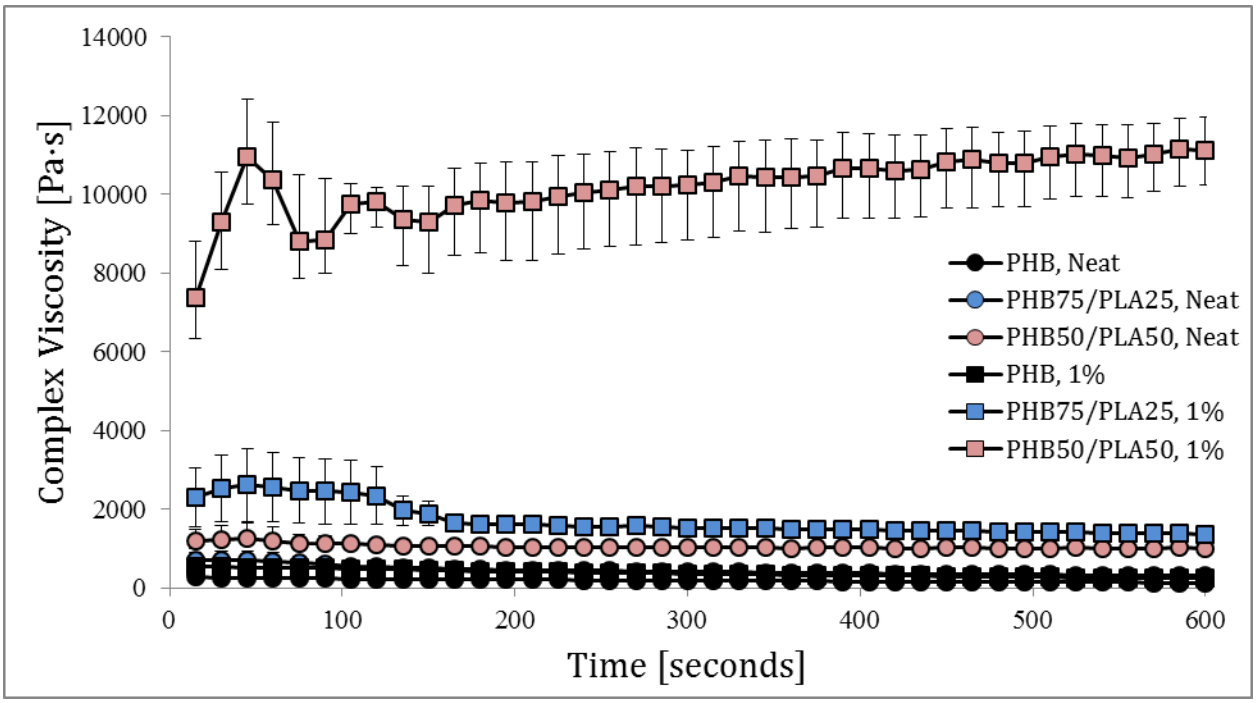

Figure 5.18: Complex viscosity of 100% PHB, 75% PHB/25% PLA and 50% PHB/50% PLA, neat and with 1% Joncryl

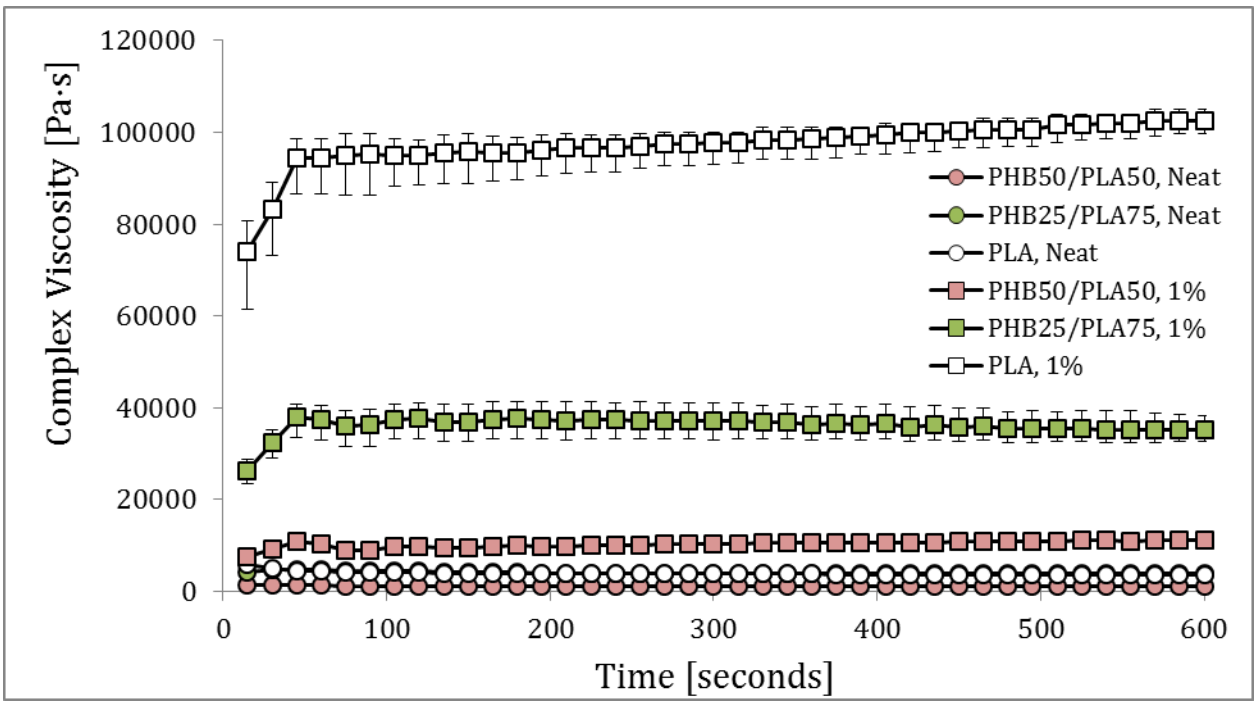

Figure 5.19: Complex viscosity of 100% PLA, 25% PHB/75% PLA and 50% PHB/50% PLA, neat and with 1% Joncryl

5.2.2 Mechanical Properties of PHB-PLA Blends

Table 5.1 shows the modulus, stress and strain at yield, and the stress and strain at break for PLA- PHB samples. No yield stress or yield strain is shown for 100% PLA with 1% Joncryl because the sample broke before it yielded. The results suggest that morphology has a significant influence on the tensile properties of the blend, and that Joncryl may act as a compatiblizer between the two polymers.

As shown in Figure 5.20 the effect of interfacial adhesion on Young's modulus can be estimated from the Kerner-Uemura-Takayangi model, which models the Young's modulus of blended semicrystalline polymers based on the elastic modulus and Poisson coefficients of the individual polymers as well as their volume fraction (Kerner, 1956) (Uemura & Takayanagi, 1966).

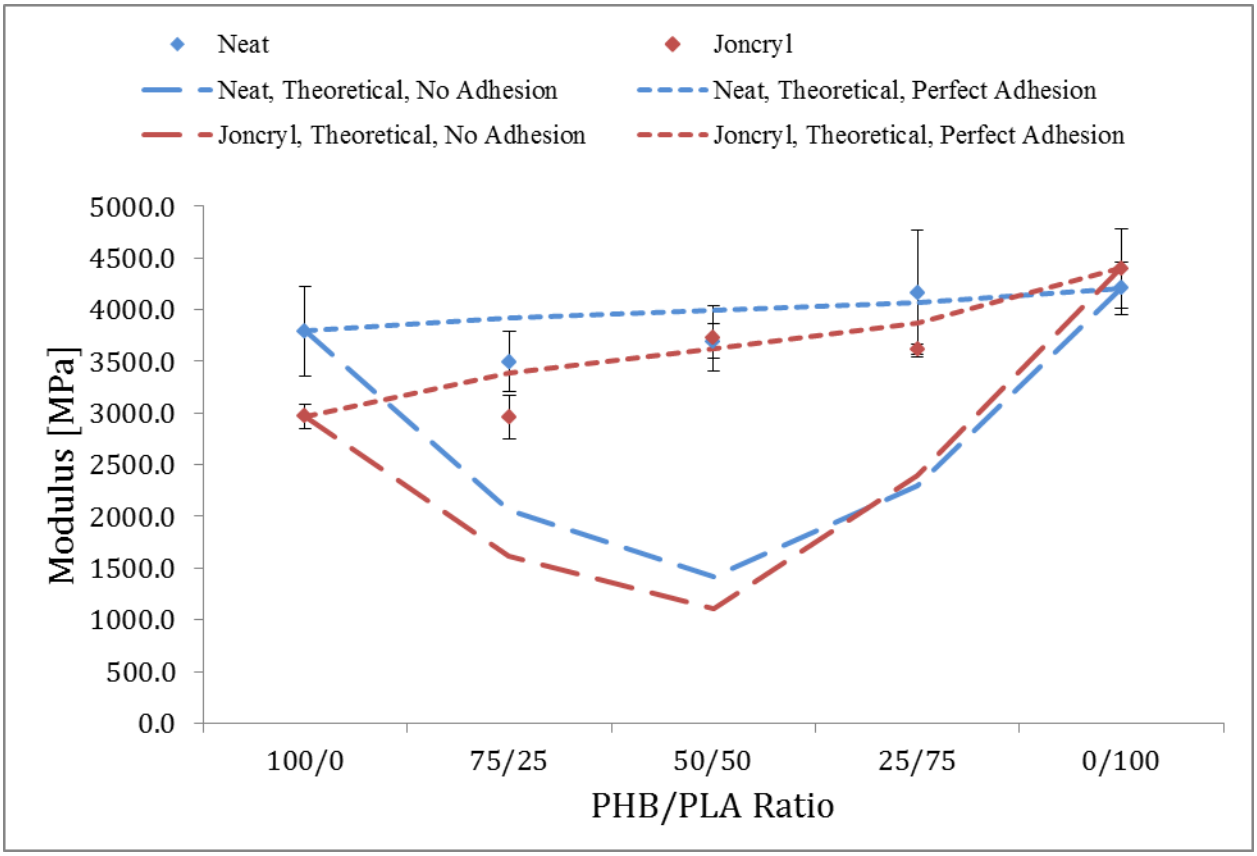

Figure 5.20: Young's modulus of PHB/PLA blends plotted as a function of blend composition, with Kerner-Uemura-Takayanagi model superimposed

The model predicts the elastic modulus of the blend for two cases: no adhesion between droplets and continuous matrix, shown as Equation 5.1, and perfect adhesion between the two phases, shown as Equation 5.2. In these equations, E_c and E_d represent the Young's modulus of the continuous phase and the dispersed phases, respectively. These were assumed to be equal to the Young's modulus calculated for unblended samples of the relevant polymer. v_c is the Poisson coefficient of the continuous phase, and ϕ_d is the volume fraction of the droplets. Based on similar work performed with blends of PLA and PCL (Broz, VanderHart, & Washburn, 2003), the Poisson coefficient was assumed to be 0.5 while the volume fraction was assumed to be equal to the mass fraction of the minor component in the blend divided by the density ratio between the two component polymers. In the case of the 50% PHB/50% PLA blend, it is not clear whether the continuous phase is composed of PHB or of PLA, and since the identity of the continuous phase affects the model, two results are possible depending on which phase is taken as continuous. In the figure, the best case estimate is presented.

Equation 5.1: Kerner-Uemura-Takayanagi model with no adhesion between phases

$$E = E_c \frac{(7 - 5v_c)E_c - (7 - 5v_c)E_c\phi_d}{(7 - 5v_c)E_c + (8 - 10v_c)E_c\phi_d}$$

Equation 5.2: Kerner-Uemura-Takayanagi model with perfect adhesion between phases

$$E = E_c \frac{(7 - 5v_c)E_c + (8 - 10v_c)E_d - (7 - 5v_c)(E_c - E_d)\phi_d}{(7 - 5v_c)E_c + (8 - 10v_c)E_d + (8 - 10v_c)(E_c - E_d)\phi_d}$$

Generally, the model indicates good adhesion between phases, possibly due to polar-polar or hydrogen-bonding interactions between acyl groups in PHB and PLA at the interface. The interaction is weakest in the 75% PHB/25% PLA phase, although the reason for this is not immediately clear and the difference is not great. It should be noted that the Kerner-Uemura-Takayanagi prediction is less likely to be reflective of interfacial adhesion when the Young's modulus of the two homopolymers are close to the same magnitude, as is the case here. Consequently, it is unclear whether the model accurately reflects the quality of adhesion between phases. Also, SEM images of the 50% PHB/50% PLA suggest that morphology may be more complex than the simple droplet-matrix morphology used to develop this model.

Despite the suggested quality of adhesion between phases, the neat blends have lower strain at break than either of the neat unblended polymers. Clearly, the presence of droplets weakened

these blends. One explanation for this phenomenon is that the droplets might not have deformed to the same extent as the continuous phase, resulting in cavitation at the droplet-matrix interface which then leads to crack formation.

Table 5.1: Results of tensile testing of PHB-PLA Blends

		100% PHB	75%PHB/ 25%PLA	50%PHB/ 50%PLA	25%PHB/ 75%PLA	100% PLA
Young's Modulus (MPa)	Neat	3790 (435)	3497 (295)	3692 (168)	4157 (614)	4205 (258)
	Joncryl	2967 (121)	2963 (212)	3724 (319)	3617 (54)	4397 (384)
Tensile Stress at Yield (MPa)	Neat	43.0 (4.0)	46.32 (0.2)	48.60 (1.0)	59.31 (4.3)	75.4 (4.1)
	Joncryl	47.1 (1.7)	51.0 (3.11)	56.2 (5.6)	62.6 (6.7)	n/a
Tensile Strain at Yield (%)	Neat	3.4 (0.3)	2.0 (0.1)	1.8 (0.01)	2.0 (0.1)	2.6 (0.2)
	Joncryl	3.6 (0.2)	3.6 (0.4)	2.4 (0.1)	2.2 (0.2)	n/a
Tensile Stress at Break (MPa)	Neat	35.5 (7.1)	43.9 (3.9)	50.7 (4.0)	54.0 (6.3)	64.6 (11.3)
	Joncryl	39.9 (7.6)	48.2 (2.6)	51.6 (5.3)	54.0 (8.7)	79.9 (14.5)
Tensile Strain at Break (%)	Neat	4.9 (1.1)	2.1 (0.1)	1.9 (0.1)	2.5 (0.4)	3.9 (1.1)
	Joncryl	4.5 (0.5)	4.3 (0.6)	2.8 (0.4)	3.4 (0.4)	2.7 (0.4)

When mixed with Joncryl the same blends demonstrate improved strain at yield and at break, although the stress at these points is not changed. The 25% PHB/75% PLA blend had a similar although less pronounced increase in strain at yield and at break. By contrast, Joncryl does not have a significant effect on either the strain at yield or the strain at break of PHB, and makes PLA more brittle. The improvement in strain for the blends can therefore not be attributed to improvement of either polymer but is more likely to be related to improvement of the interfacial properties.

Although Joncryl reduced the Young's modulus of PHB, the polymer did not become significantly more ductile. Meanwhile, addition of Joncryl to PLA made the polymer significantly more brittle. The fact that the polymer did not yield suggests that it may even have

crosslinked. This is substantiated by the change in storage modulus between neat PLA and Joncryl-added PLA, shown in the Appendix A7.

Chapter 6 Discussion

In the three years of PHB research which are accounted for in this work, very little progress has been made. This can in part be traced to poor assumptions or faulty experimental protocol, but it must be admitted that some of the obstacles faced in this endeavor were totally unexpected and have yet to be fully explained.

6.1 On the Failure of Chain Extender-PHB Reaction

In light of the structural similarity of PHB and PLA, the discrepancy in complex viscosity response to the addition of Joncryl is striking: at a loading of 1% by weight of Joncryl, PHB had slightly elevated complex viscosity while PLA appears to have crosslinked. It is supposed that the contrast can be attributed to the consequences of thermomechanical degradation, for three reasons. First, degradation yielded new carboxylic acid groups, increasing the number of reactive sites which might have bonded with Joncryl, reducing the likelihood that a single PHB chain might react with two different Joncryl molecules to form a network. Second, degradation is due to an intramolecular reaction which is unaffected by the end groups of the polymer, so chains which had already bonded with Joncryl might continue to degrade. Third, degradation produced acrylate-terminated polymer chains, which are unreactive with conventional chain extenders.

6.2 Influence of Bond Rotation Barrier on Degradation

The fact that degradation is intramolecular, requiring the bond rotation to the kinetically less favorable cis-configuration, means that degradation could conceivably be prevented by increasing the barrier to bond rotation. In the literature, only one attempt at reducing the rotation of PHB has been reported. In this experiment, phenylene bisoxazoline was grafted to PHB in a branching position. The modified polymer was compared to the original using TGA, and it was found that the modified polymer degraded at a higher temperature. However, as has already been mentioned in this document, TGA results do not accurately portray thermomechanical degradation and consequently it is unclear whether this is an effective solution to thermomechanical degradation (Liu Q. , Zhu, Wu, & Qin, 2009).

6.3 Thiols as Chain Extenders

A study of acrylate-active compounds was undertaken in order to see if they might act as chain extenders in PHB. Unlike alcohols and carboxylic acids, which typically appear on polyester chains, acrylates are not intended to react with conventional chain extenders. As degradation of PHB occurs, acrylate-terminated PHB chains accumulate in the absence of any favorable reaction sites. By contrast, alcohol- and carboxylic acid-terminated chains react with one another in order to maintain equilibrium and consequently their population does not accumulate at a comparable rate to acrylate-terminated chains. If an acrylate-reactive compound were added to the mixture, perhaps it would be able to scavenge acrylate-terminated chains and reincorporate them onto non-acrylate chains, thereby reversing the effects of degradation.

Fortunately, acrylate chemistry is commonly exploited for a number of applications, often using the well-known Michael reaction, shown below in its most generic sense. Here, EWG refers to electron-withdrawing group, which in the case of an acrylate is the ester. A number of different compounds will react in acrylates in this way, including nitrogen, oxygen and sulfur compounds (Wabnitz & Spencer, 2003). Thiols in particular are known to react effectively with acrylates in a variation of the thiol-ene 'click' reaction. These reactions are often catalyzed by weakly nucleophilic amines or phosphates (Lowe, 2009) (Chan, Hoyle, Lowe, & Bowman, 2010).

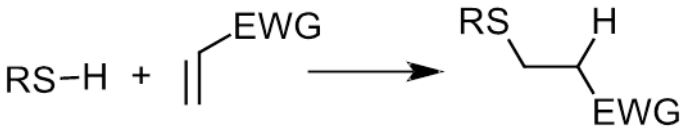

Figure 6.1: Michael addition of thiol (Lowe, 2009)

Of course, the reactions cited in literature were all performed in solution at room temperature, conditions which are not at all comparable to bulk reactions at 180^{o}C. This is a common problem for polymer research: it is generally easier to perform a reaction successfully in solution, but the results are not always valid for typical processing conditions. While a large body of literature exists on thiol-ene reactions, almost all of it appears to be performed close to room temperature (Mather, Viswanathan, Miller, & Long, 2006) (Hoyle & Bowman, 2010).

Ultimately, two thiols were selected in part based on their reactivity in thiol-ene reactions and in part on the possibility that they might react with alcohols or carboxylic acids, thereby linking the

acrylate chains back to non-acrylate chains. Pentaerythritol tetrakis(3-mercaptopropionate) contains four thiols as well as four ester functionalities which might link to PHB via transesterification. The other thiol, namely 6-mercapto-1-hexanol, contained an alcohol and a thiol, so that once the thiol reacted the alcohol might attack a carboxylic acid on another PHB chain. In addition, tris(nonylphenyl)phosphite was already available in the lab, and so this was tested as a phosphorous catalyst for Michael addition.

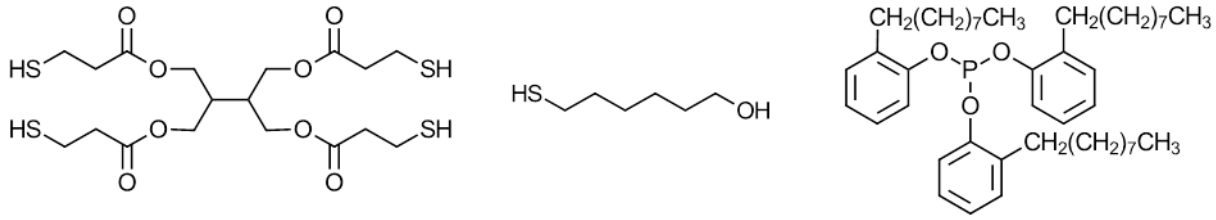

Figure 6.2: Pentaerythritol tetrakis(3-mercaptopropionate), 6-mercapto-1-hexanol and Tris(nonylphenyl)phospite

In order to evaluate the effectiveness of thiols with PHB, each compound was mixed with the polymer at a concentration of 2%. The effect of the phosphite catalyst was also evaluated by producing mixtures of PHB with 2% of each of the thiols as well as 0.5% of the phosphite, where percentages are mass relative to mass of PHB. During the period where these experiments were performed, reliability was an issue, and consequently all the samples were produced on the same day. Issues with reliability are explained in Appendix A2.

The complex viscosity of these samples is shown in Figure 6.3 as a function of time, in comparison to neat PHB. None of the samples appeared to have much more than a marginal increase in complex viscosity over neat PHB, and in fact most samples have reduced complex viscosity. In the opinion of the researchers, the project did not merit further exploration given the amount of time available and the likelihood of success with continued efforts.

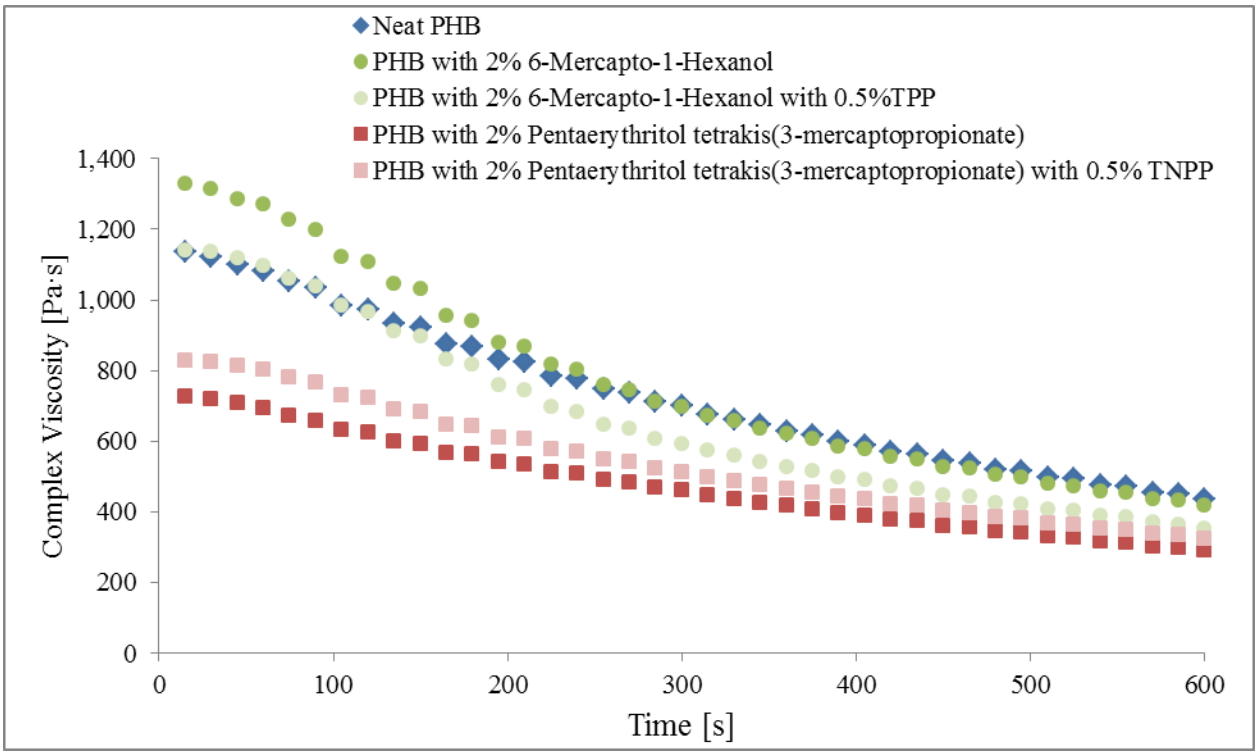

Figure 6.3: Complex viscosity of thiol-PHB mixtures

6.4 Lack of Reproducibility in Polymer Compounding

As discussed in the Experimental section, sample reproducibility depended upon control of temperature and shear history during processing and moulding. In practice, this proved more challenging than anticipated. Originally, the samples were intended to be compounded in the Brabender mixer then moulded in the hot presses located in the polymer processing lab at the École Polytechnique. The process required a relatively high amount of manual input: the entire polymer sample could not be loaded in the hopper at once, and so the pellets had to be gradually added to the mixer by hand; the mixer had to be stopped manually after the desired mixing time; often, either the software would malfunction and close unpredictably without saving or the Brabender would stop delivering torque to the rotors; teflon sheets used to protect the polymer during compression-moulding were often missing, requiring the use of old and sometimes dirty sheets, or use of often ineffective aluminium foil in its place; the hot press pressure was controlled manually, had an unreliable pressure gauge and leaked oil; once hot pressing was complete the sample had to be removed and carried to another press while hot in order to be cooled to room temperature; finally, the cold press also had an unreliable pressure gauge. In addition to these inherently unreliable manual inputs, the Brabender was used for many different experiments with a range of polymers and chemical compounds. This may have played a role in reducing reproducibility in cases where the surfaces of the mixing chamber were not properly cleaned, contaminating subsequent experiments. To avoid contamination the mixing chamber was purged before and after sample preparation, but evidence of contamination in some samples suggests that purging was not always effective.

While experience mitigated problems of control, a satisfactory protocol was not developed until sample production was moved to the ETS facility, where equipment was automated to a greater extent. The Haake mixer at ETS could be programmed to start and stop automatically based on temperature and time settings, and could load an entire sample in one shot, using a heavy piston to force the polymer into the mixing chamber. Also, there were no other users of the equipment, reducing the likelihood of contamination from other users. The same press was used for heating and cooling, and pressure and temperature were set automatically. All of these advantages reduced the likelihood of user error and consequently led to increased reproducibility. This is demonstrated in Appendix A2.

6.5 PHB Insolubility

As has been noted in this work, the grade of PHB used was not soluble in chloroform, a fact that considerably complicated its analysis. Of course, complete dissolution of a polymer in a solvent is a necessary condition for size exclusion chromatography, and is a facilitating condition for mass spectrometry, proton magnetic resonance spectrometry and infra-red spectrometry. In practice, any direct measurement of molecular weight is impossible unless the polymer can be dissolved in a solvent. Of comparable importance is the acid test, through which the number of alcohol and carboxylic acid groups in a sample is quantified. This latter experiment can be used to determine the effectiveness of chain extenders as well as the extent of degradation.

According to literature, PHB is generally dissolved in chloroform. However, PHB has been known to dissolve in other solvents, including dimethylformamide (referred to here as DMF), and ethyl acetate. Attempts were made to dissolve PHB in chloroform, ethyl acetate and DMF with little success. First, the polymer-solvent mixture was placed in a reflux apparatus and heated to its boiling point. In the case of chloroform, polymer pellets broke down into millimeter-scale grains which persisted indefinitely, while in the case of the other solvents no change was observed to the polymer. Since reflux did not have an effect, the samples were then placed in an ultrasonic bath in the hope that agitation might encourage dissolution of the polymer. Sonic agitation was found to produce enough heat to boil water, causing the sealed chloroform samples to boil, then burst and become contaminated with water. The apparatus was consequently modified to stabilize the container and introduce a heat sink (an aluminum basin of ice water) above the ultrasonic bath. The bath was then operated at a controlled temperature for as long as a week, but solubility was not observed.

It is supposed that the manufacturer performed some operation on the PHB which rendered it insoluble in chloroform, although the nature of this operation remains unclear. Determining if and how the polymer might be dissolved would serve any future attempts to monitor molecular weight, or in the event that a solvent-cast film is desired.

One step which might contribute to an explanation of the lack of solubility would be to characterize the millimeter-scale grains which persisted in chloroform, although it is unclear what their composition might be. It should be noted that the manufacturer reports adding an

unspecified antioxidant and nucleating agent, which might be characterized from the insoluble grains.

6.6 Unexplored Properties of PHB/PLA Blends

6.6.1 PHB/PLA Blend Morphology

Because this work was intended to examine a wide range of blend composition, some PHB-PLA blend properties were not investigated in detail.

There is a suggestion that the decay of complex viscosity as a function of time varied depending on the ratio of PHB to PLA in a given blend. When the complex viscosity curves were modeled as first-order reactions, the rate constant varied depending on the blend composition, as shown in Table 6.1 below, with the 100% PHB and the 75% PHB/25% PLA blend having rates of decay an order of magnitude higher than the decay of the 50% PHB/50% PLA, 25%PHB/75% PLA and 100% PLA samples.

Table 6.1: Rate of decay of PHB/PLA samples

Blend Composition	1st Order Rate Constant (×104 s-1)
100% PHB	-9.75
75% PHB/25% PLA	-13.2
50% PHB/50% PLA	-1.58
25% PHB/75% PLA	-2.60
100% PLA	-2.42

Although there is at present no physical explanation for this phenomenon, it might merit a more thorough study of morphology and rheology. The behavior of the 50% PHB/50% PLA blend is especially curious – not only does it decay at a slower rate than other blends, but its complex viscosity was much noisier than that of other blends. As discussed in Appendix A7 and A8, the 50% PHB/50% PLA blend was briefly investigated.

Further study of PHB/PLA blends might begin with frequency sweeps of the relevant blends, to determine if any significant changes occur in the relaxation spectrum as a function of blend composition. A frequency sweep of PHB had been attempted, but in the time required to complete even a rudimentary sweep the polymer degraded so much that the results were not perceived to be useful. However, the much slower decay of the 50% PHB/50% PLA means that

degradation probably would not interfere with a frequency sweep. This experiment would provide valuable information about the types of long-range coupling occurring within the sample. Coupled with SEM images of microtomed PHB/PLA blends, it might be possible to determine a morphological explanation for the disparity in complex viscosity decay in these blends.

6.6.2 Joncryl-Polymer Interactions in PHB/PLA Blends

It is unclear whether the two polymers compete for reaction with Joncryl, or if Joncryl reacts preferentially with one over the other. Further, the optimal quantity of Joncryl appears to differ between the two polymers: PHB appears to be only slightly affected by 1% by weight of Joncryl while PLA is crosslinked. It might be worthwhile to produce a masterbatch of PHB with Joncryl and then add PLA once the majority of the Joncryl has reacted with PHB, so that while the majority of the Joncryl reacts with PHB, some small quantity of the chain extender is left to act as a compatibilizer between PHB and PLA.

A more conventional examination of PHB-PLA blend is a study of isothermal crystallization of the blends with Joncryl. Isothermal crystallization studies have already been performed on PHB-PLA blends which determined that except for at very low concentrations of PHB, the two polymers do not affect each other's crystallization kinetics (Hu, Sato, Zhang, Isao, & Ozaki, 2008). While the effect of Joncryl on crystallization can at present only be speculated, it is suspected that Joncryl reduces the stability of PHB crystals.

6.6.3 Co-Continuous PHB/PLA Blends

Another phenomenon of PHB-PLA blends that was not explored was a micrograph of 50% PHB/50% PLA that seemed to suggest co-continuity shown in Appendix A6. The micrograph could not be reproduced, and consequently the subject was not pursued. However, co-continuity appears not to have been explored or even identified in the literature. Co-continuity could be determined through extraction gravimetry analysis if an appropriate solvent could be found (Badhane, Champagne, Huneault, Tofan, & Favis, 2006). The insolubility of PHB suggests that a range of solvents could be applicable. For instance, Toluene is reportedly effective for selective etching of PLA/PHB blends (Zhang, Xiong, & Deng, 1995).

Chapter 7 Conclusion

This experiment sought to reduce thermomechanical degradation of PHB through the use of chain extenders. The grade of PHB available for the experiment proved to be insoluble in all available solvents, and consequently the molecular weight chance of the polymer was inferred from complex viscosity. Chain extenders selected for the experiment were intended to cover a wide range of chemical reactions in order to give some indication of which chemical functionality was most effective with PHB. Although complex viscosity responded in some cases to chain extenders, the degradation rate was not affected by chain extension.

Originally, the goal of the project had been to explore the mechanical properties and blend morphology of the improved PHB-based material. None of the materials met the criteria set for an improved material. The Joncryl-PHB system, which performed better than the other chain-extender-PHB system, was further characterized despite not having met the original criteria for success. The system was blended with another biodegradable polymer, PLA, and subjected to tensile testing. The morphology of the neat blend was found to consist of coarse droplets with seemingly weak interaction between matrix and drops. Addition of Joncryl significantly reduced droplet size, a change which manifested itself as increased stress at yield and increased strain at break, as well as increased strain at yield for the 50% PHB/50% PLA and 75% PHB/25% PLA blend.

The Young's modulus of blends corresponded to the Kerner-Uemara-Takayanagi model for strong adherence between droplets and matrix. However, the similarity of the Young's moduli of the two homopolymers reduces the validity of the model. Even if the model is taken as valid, low strain at yield and strain at break suggest that droplets probably do not deform with the matrix, leading to cavitation. If Joncryl were to bond with both PHB and PLA, it would increase the strength of interfacial interaction by providing a chemically bonded bridge between the two phases. This hypothesis might explain the increase in strain at break and at yield experienced by PHB-PLA blends with addition of Joncryl.

Improvements to the mechanical properties and degradation resistance of PHB and PHB-PLA blends which have been presented in this work are marginal at best. The role of Joncryl in these blends is, to this point, unclear. However, a practical protocol has been established, through which further experiments on PHB and PHB-PLA blends, as well as any other PHB blends,

might be performed. It is recommended that any further research concern itself with determining the reasons why the reactivity and solubility of the PHB used in this study did not conform either to expectations based on its chemical structure, or based on prior literature.

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List of Appendices

Appendix A1: Glossary of Equation Symbols

M_{nt}	Number average molecular weight at a given time
M_{no}	Number average molecular weight at a reference time
k	Reaction rate constant
t	Time
η^*	Complex viscosity
A	Proportionality constant
M_W	Molecular weight
α	Power-law constant
ω	Frequency
$\dot{\gamma}$	Strain rate
η	Viscosity
$\eta(T)$	Viscosity at a given temperature
η_0	Viscosity at a reference temperature
E_a	Activation energy
R	Ideal gas constant
T	Temperature
$\hat{T}$	Torque
$\hat{T}_0$	Torque at a reference temperature
E	Elastic modulus
E_c	Elastic modulus of the continuous phase
v_c	Poisson ratio of the continuous phase
E_d	Elastic modulus of the dispersed phase
ϕ_d	Volume fraction of the dispersed phase
ρ	Pearson correlation coefficient
X_i	Data point i in data set X
$\bar{X}$	Average of all points in set X
Y_i	Data point i in data set Y
$\bar{Y}$	Average of all points in set Y
s_x	Standard deviation of set X
s_y	Standard deviation of set Y

Appendix A2: Reliability in Compounding

Effect of Compounding on Reliability

As explained in the discussion section, reproducible sample preparation was complicated by degradation during processing. PHB degradation is principally a function of temperature, so developing a reproducible protocol necessarily involves controlling the thermal history of the polymer as closely as possible. If the thermal history of samples is kept as similar as possible, they should all degrade to roughly the same extent.

In practice, the most difficult aspect of sample preparation to control is compounding. Due to the high viscosity and high Prandtl number of PHB, the temperature of the mixing chamber during compounding is very difficult to control or measure. The process is further complicated by the fact that the polymer must be added as solid pellets and melted during processing, meaning that the mixture is heterogeneous during the first two or three minutes of compounding.

Ultimately, process control during compounding consists of ensuring that the strain applied to the polymer is the same in every case by maintaining the rotors at a set speed and regulating pellet loading rate to ensure that the melting phase is reproducible. The protocols for compounding are outlined below.

École Polytechnique de Montréal (Brabender)

The Brabender used initially at École Polytechnique was difficult to operate reliably for a number of reasons which have already been listed in the discussion section:

- lack of a hopper or effective method to close the mixing chamber, loading the chamber to quickly resulted in pellets being shot out of the chamber or an overflow of the heterogeneous mixture of unmelted pellets and molten polymer;
- recording software which was programmed to begin recording when torque reached some threshold, which was inevitably reached while loading was in progress but the point at which the trigger occurred was unpredictable;
- occasional unannounced cessation of torque without explanation;

- recording software crashes or failure to record, especially disconcerting because mixing time was based on the software (experiments were also timed by chronometer to avoid this problem, but the loss of torque data was problematic).

In addition, the processing equipment was overused. In a given month, it was possible with luck to reserve 4 or 5 nonconsecutive days for processing. When other users cancelled reservations, it generally not possible to make use of the vacated time because the polymer had to be dried for 12 hours before use and dryer space was too limited to be permanently drying PHB. The fact that so many students use the Brabender also meant that the mixing chamber was often poorly cleaned. This necessitated at least one, and sometimes two, purges of the mixing chamber with polymethyl methacrylate provided for this purpose before sample preparation.

The protocol for Brabender processing went as follows:

1. The mixing chamber is reassembled and heated to 175^{o}C
2. The recording software is started, it sends the user a request start the rotors so that it might calibrate its torque reading
3. The user sets the RPM setpoint for the rotors into the Brabender, starts the rotors and confirms this to the recording software
4. The recording software then notifies the user that it is ready to begin the experiment, at which point the user is meant to load the chamber
5. The chamber is gradually loaded with 24g of polymer pellets over a period of 120 seconds, during which time the recording software records a change in torque and begins recording;
6. The polymer is compounded for ten minutes, and then the rotors are stopped, and the mixing chamber opened
7. As much polymer as possible is removed with a brass spatula and placed in the appropriate mould for pressing
8. Any polymer which happens to fall onto the table or ground is inevitably contaminated by dirt and is thrown away
9. The mixing chamber is cleaned

The turnaround time for a compounding session – which is to say the time required to heat the mixer, compound the sample for the required time, empty the polymer, cool the equipment to a safe temperature, clean the equipment and begin reheating – is approximately an hour. With the purges necessary at the start and finish of a day's work, six compounding sessions on the Brabender could easily take more than eight hours. If one of those mixing sessions encountered an unexpected computer crash, as was generally the case, a day of sample preparation generally yielded five compounding sessions. With a mixing chamber volume of 30 cubic centimeters, this corresponds to 150 cubic centimeters of compounded polymer, or 5 batches of six rheology samples.

École de Technologie Supérieure (Haake)

Fortunately, in the autumn of 2012 it became possible to use the newly-opened polymer processing lab at ÉTS. In this facility, compounding was performed in a Haake compounder having a much larger mixing chamber of as well as much more sophisticated controls. More importantly, only two other groups used the equipment, meaning that the Haake could be used as much as needed, and that the risk of contamination was greatly diminished. Another advantage of the Haake was that pellets were loaded into the mixing chamber through a long tube which could hold an entire load without overflowing. The tube was covered by a heavy piston, which forced the pellets into the mixing chamber without any manual input. At a mixing chamber volume of 310 cubic centimeters, one compounding session lasting one hour could produce more samples than an entire day of compounding at École Polytechnique.

On the Haake, the compounding process went as follows:

1. The mixing chamber was assembled and the relevant equipment was turned on
2. The software controlling the heating elements was set to heat the mixer to 175^{o}C
3. The rotors are set to begin rotating at 60RPM as soon as the temperature of the mixer is within 0.5^{o}C of 175^{o}C
4. Once the rotors start turning, the pellets are all loaded into the chamber at once and the piston is dropped onto the pellets
5. The software begins recording as soon as torque reaches 60 Newton-meters, which was identified in a calibration test as the peak torque reached by PHB during melting

6. As the polymer melts, the piston closing the mixing chamber sinks under its own weight to its maximum depth and locks into place, holding the volume of the mixing chamber constant
7. Compounding continues for 10 minutes, at which point the machine automatically stops
8. The mixing chamber is opened and as much polymer as possible is cleaned out using a brass spatula

The Brabender torque-time curves for several compounding sessions on neat PHB are shown in Figure A1 below, while the analogous Haake curves are shown in Figure A2. In all cases, the protocols outlined above were followed, and the polymer was dried prior to compounding. In the case of the Brabender, results appear to be contextual, with results well-clustered for a given day of processing, but varying between different processing days. By contrast, the Haake results, which represent several different days of work, all follow a clear trend. It should be noted that some of the Haake data shown is for PHB with chain extenders added at 2:30 seconds, but this data conforms to the same trend as the neat PHB sample compounding.

These results are corroborated by complex viscosity time-sweeps. In Figure A3, rheology samples originating from Brabender-compounded polymer are shown, while Figure A4 shows analogous Haake data. In each case, a data point represents at least three samples from the same mould. For Brabender-originating data, lines represent the mean complex viscosity for data of the same colour, where colours represent samples that were produced on the same uninterrupted compounding session. Again, Brabender-originating samples seem homogeneous within a given compounding session, but each session shows its own trend. Also of note are the two relatively high complex viscosity samples, which suggest contamination. Incidentally, it is interesting that a trace amount of some contaminant might have increased complex viscosity, but since the contaminant was not identified, the phenomenon could not be exploited.

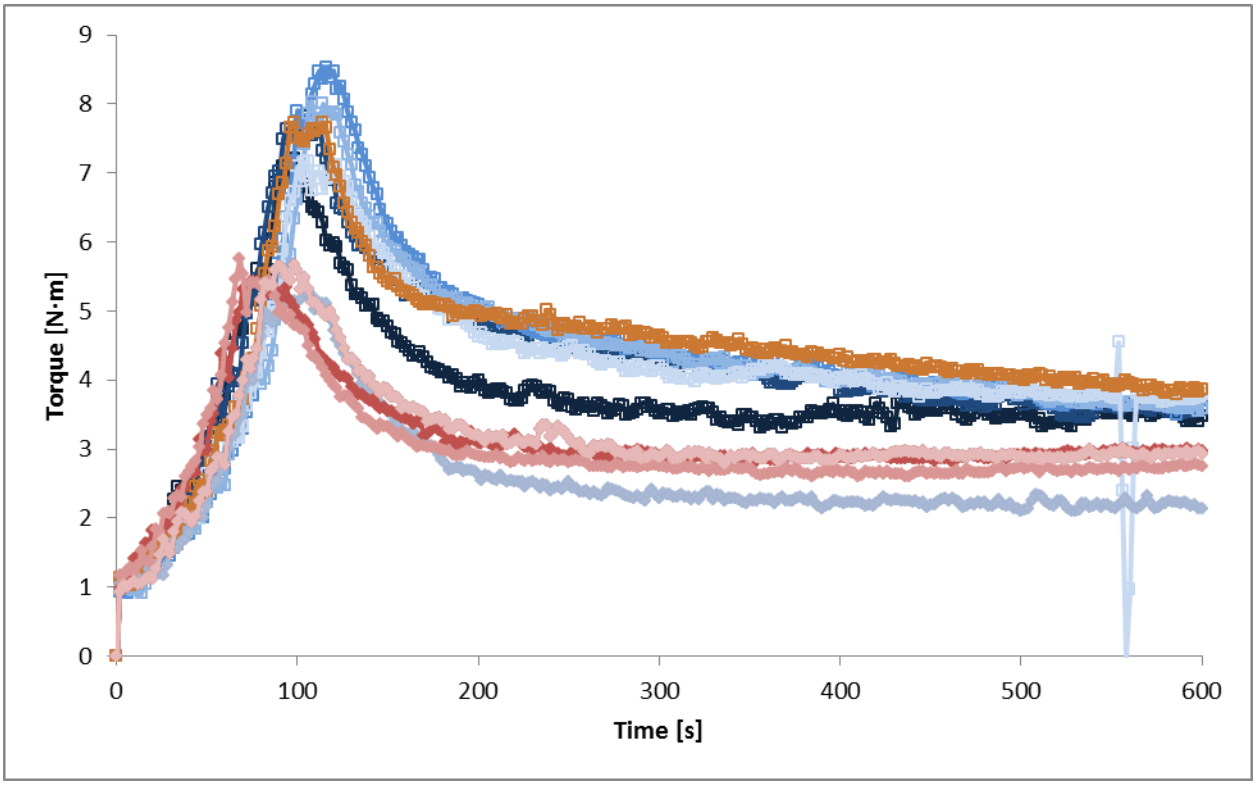

Figure A1: Torque-time curves for Brabender-produced samples. Each colour indicates data from consecutive compounding sessions

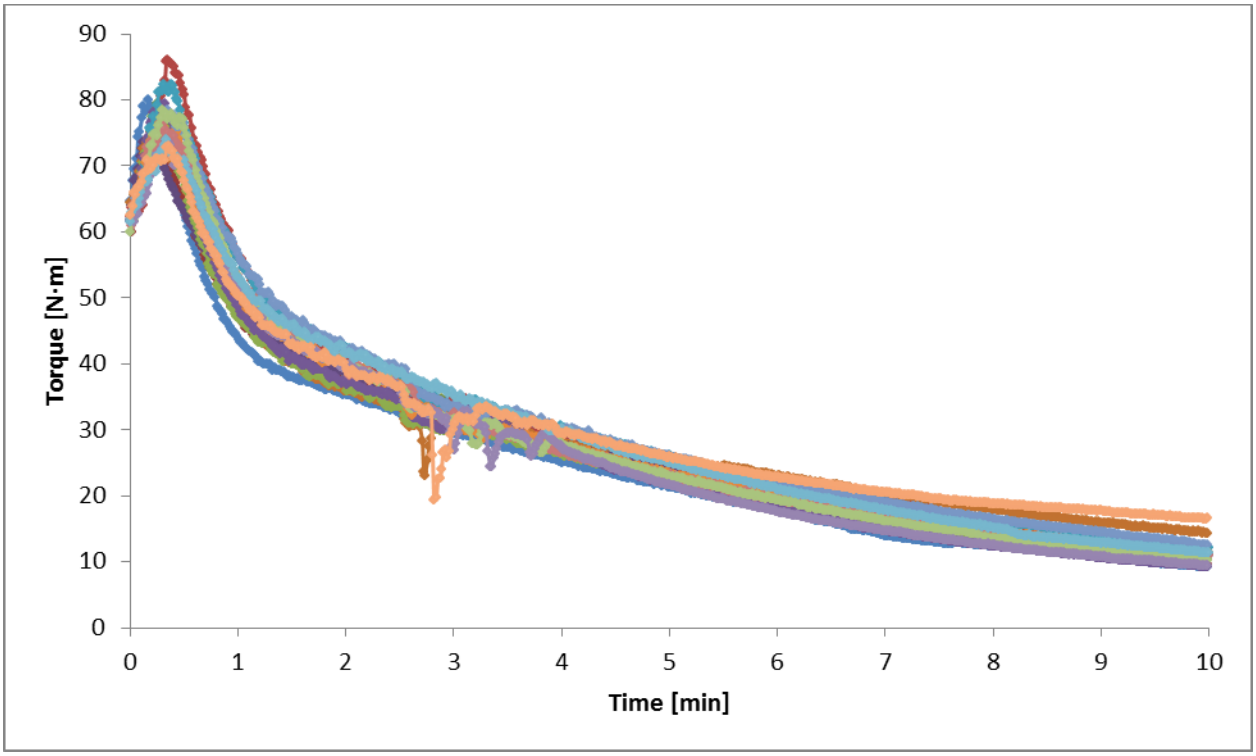

Figure A2: Torque-time curves for Haake-produced samples

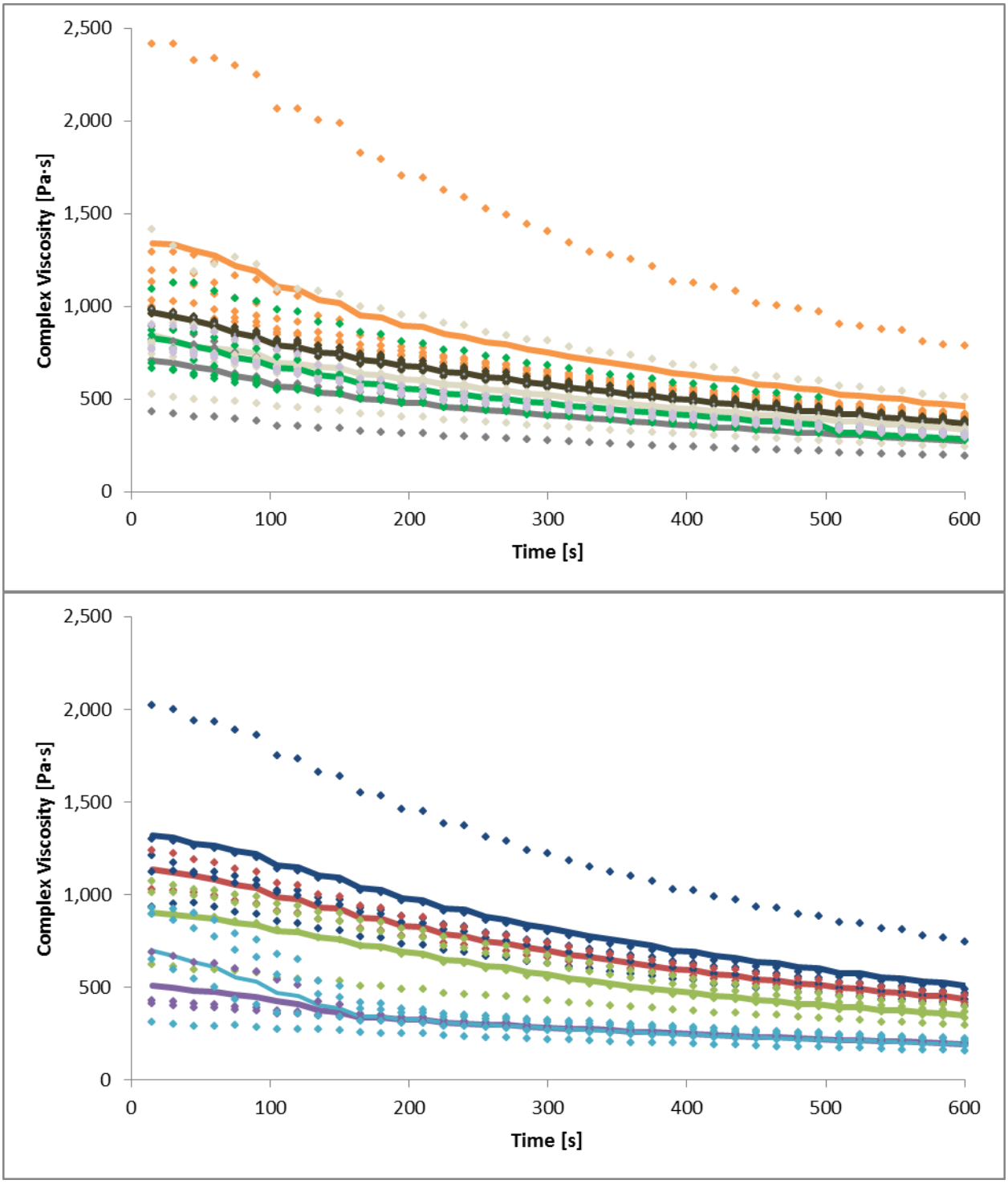

Figure A3: Complex viscosity of neat PHB originating from Brabender compounding;colours represent data from consecutive compounding sessions; data points represent average complex viscosity of several samples from the same compounding session. Results were divided into two graphs to allow the data to be more easily read

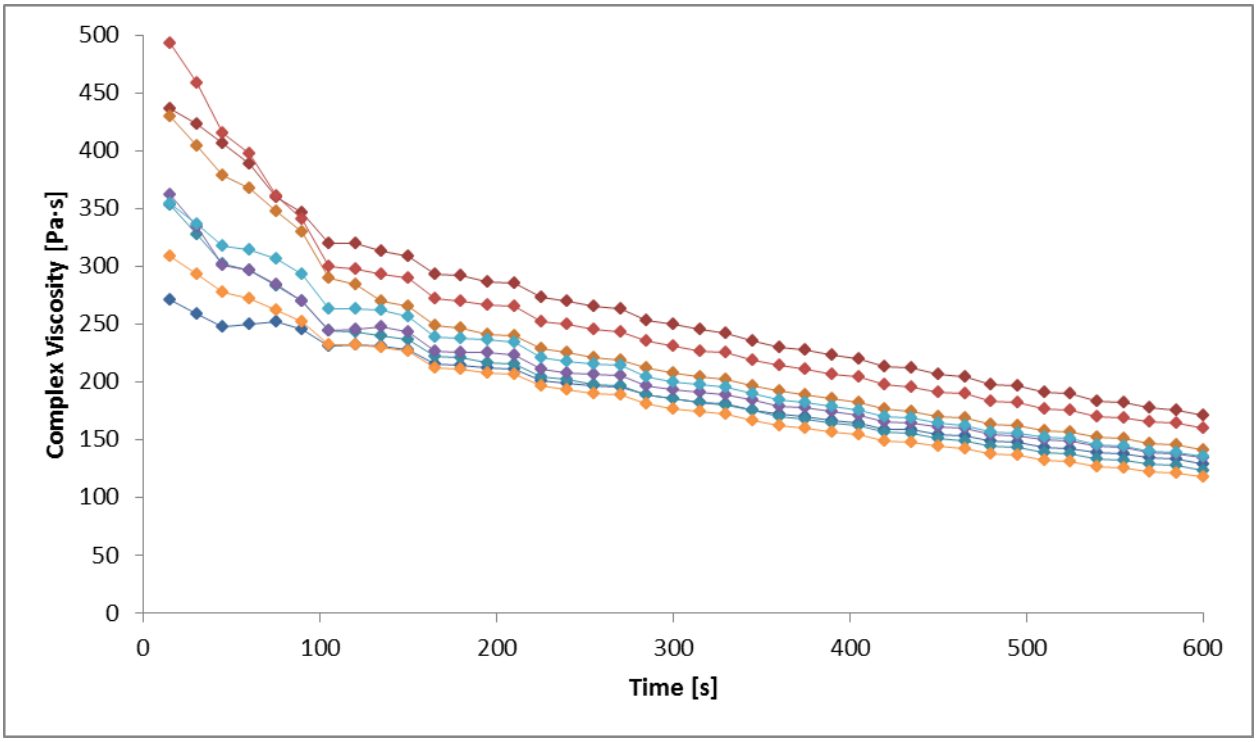

Figure A4: Complex viscosity of several neat PHB samples originating from the Haake. Each data set represents the average from several samples from the same compounding session

Appendix A3: Forays in FTIR Analysis

FTIR Investigation, Part 1: In Pursuit of Reliable Processing

In the first months of research on PHB, the primary goal had been to find quantifiable measures of degradation. FTIR was identified as an analytical method which might yield information on degradation, with the added advantage that changes in the IR spectrum could be related to molecular structure. To test the capacity of FTIR to quantify degradation, small quantities of PHB were removed from the mixing chamber at fixed intervals during compounding. The intensities of peaks in these spectra were compared to determine if a quantifiable relationship exists between degradation and IR absorption intensity. The peaks used for comparison were selected based on the correspondence of their wavenumbers to chemical bonds which might be formed or broken during degradation.

The spectra are presented in two figures showing two different segments of the FTIR spectrum. Figure A5 presents C-H stretches, while Figure A6 presents C-O and C=O. The variation in intensity does not seem to be related to compounding time, although some variation occurs between samples. The sample from 7 minutes deviates significantly in intensity from the other samples, but this does not seem to bear any relationship to residence time. Also, no new peaks are seen developing as would be the case if a chemical reaction were occurring due to the formation of new compounds. This suggests that FTIR is not detecting any change that could be conclusively related to degradation.

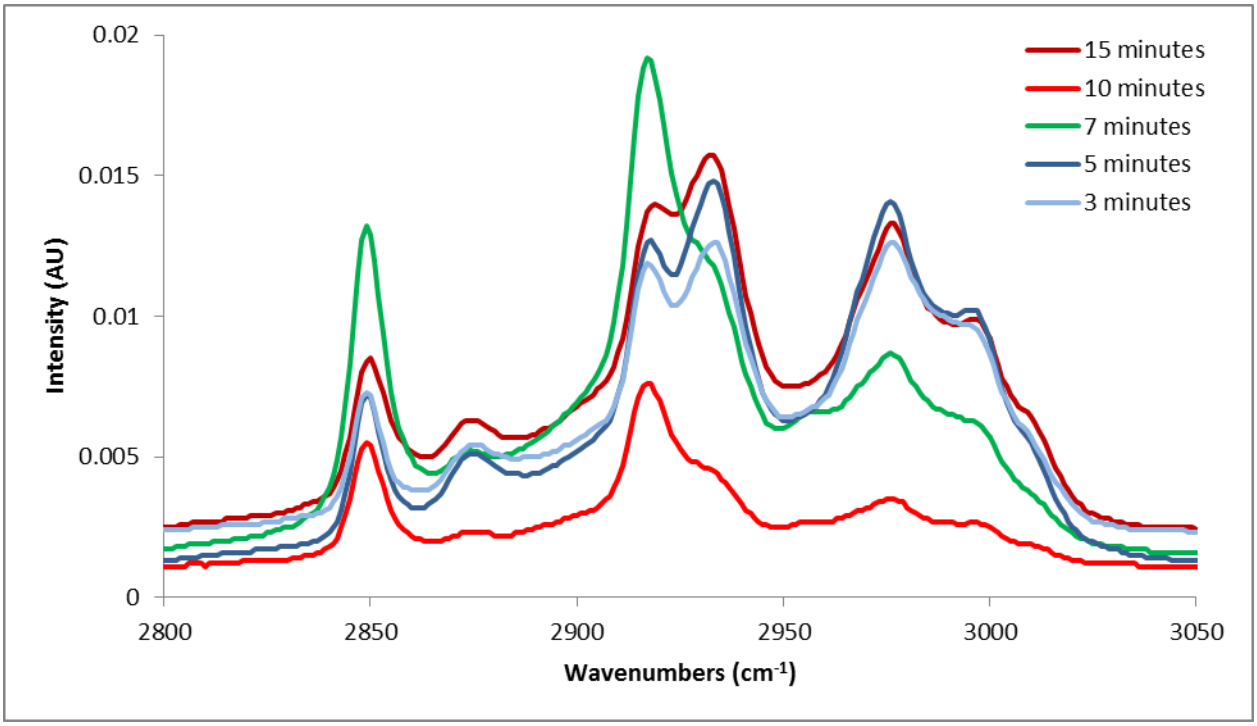

Figure A5: C-H stretch region of PHB after a range of compounding periods

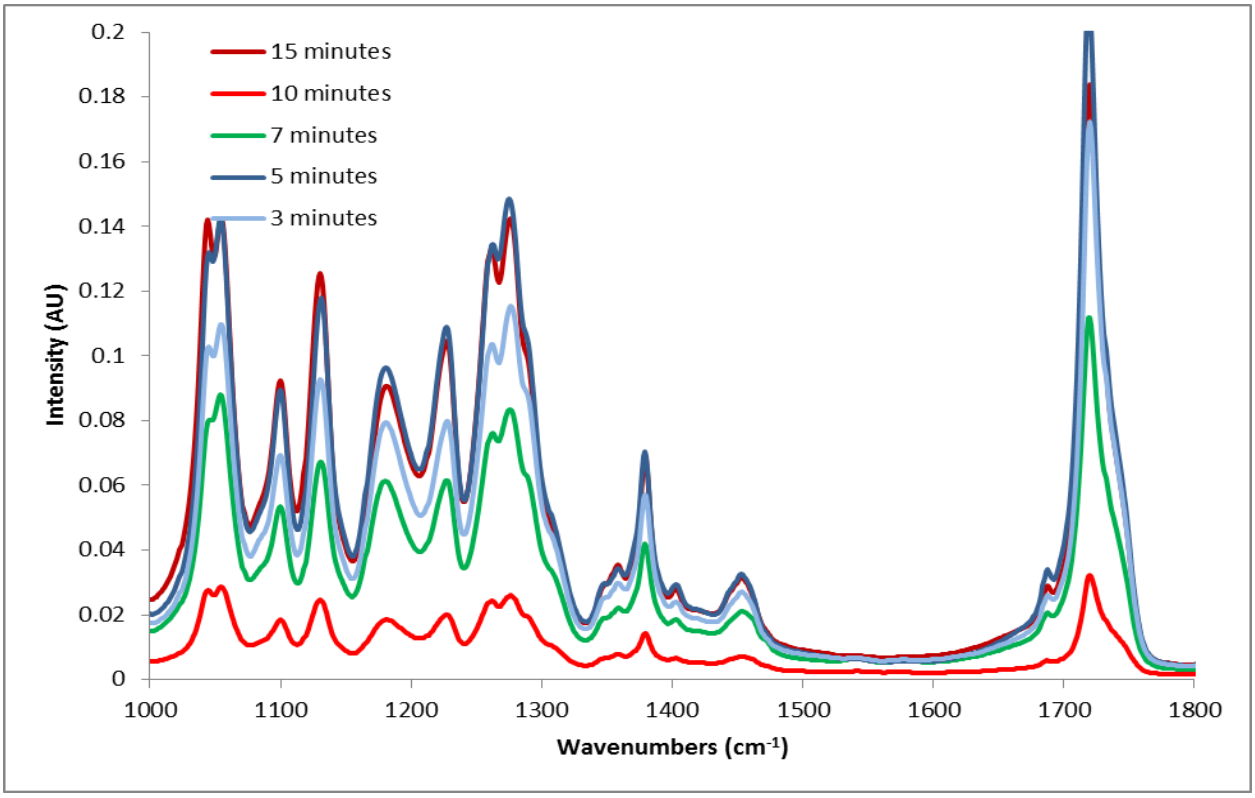

Figure A6: Ether and ester stretch region of PHB samples after a range of compounding periods

Appendix A4: Injection Moulded PHB samples

Based on the work of Leroy et al on injection moulding of PHB, it was suggested that injection moulded samples might be preferable to compression-moulded samples because residence time in the injection moulder would be less than the residence time required for compression moulding (Leroy, Petit, Audic, Colomines, & Deterre, 2012). Consequently, a brief experiment was performed on the viability of producing samples via injection rather than compression during the winter of 2013. Evaluation of the reproducibility of injection-moulded samples was performed by rheometry as well as by FTIR – while rheometry provided a more accurate analog of degradation, FTIR could potentially provide faster analysis of the samples.

The experiment was performed on the Mini-jector Model 45 'Wasp' mini injection moulding machine at ETS. In order to better understand injection moulding, a diagram of a typical injection moulder has been included below, although unlike the diagram, the barrel of the 'Wasp' is vertical rather than horizontal, with pellets loaded at the top and molds placed underneath. The operating principles remain the same, however:

1. Pellets are fed into the barrel and drawn towards the nozzle by a special screw capped by a ram, identified here as the 'nonreturn valve'
2. Between the hopper and the nonreturn valve, the polymer is melted and mixed by the screw
3. As molten polymer accumulates between the nozzle and the nonreturn valve, the screw is displaced away from the nozzle
4. The volume of molten polymer available for injection is estimated by the distance the screw has risen multiplied by the inner diameter of the barrel
5. Under automatic control, the screw will rise to a setpoint before stopping, but if there are not enough pellets in the hopper or if the pellets are too cold to melt then the screw will turn indefinitely without rising
6. When sufficient polymer has accumulated, the nozzle is pressed against the platen and the screw is driven towards the nozzle, emptying the accumulated polymer into the mold
7. The pressure driving the screw down is set to a specific value (1050 psi in this case), which dictates the rate and volume of polymer which is injected

8. The process of driving polymer out of the injection moulding machine is referred to as extrusion, although when purging extrusion also refers to the entire process of melting pellets and then ejecting them from the nozzle
9. Once pressure has been applied to the screw for a set time, the pressure is released and the nozzle is lifted off of the platen to allow the mold to be ejected

The injector operates on an automatic cycle in which injection occurs at a set pressure for a set time, followed by extrusion of new pellets until the screw rises to a set point. When, for whatever reason, automatic control failed, the subsequent experiment was rejected for reasons of reproducibility. The experimental protocol went as follows:

1. The moulder was purged with a polyolefin provided by ETS
2. During purging, a purge tube is used in place of a mold
3. The purpose of the purge tube is to allow polymer to be extruded indefinitely until the entire volume of the barrel is emptied
4. The machine was then purged with PHB until the purge polymer was no longer present in the extrudate, based on the colour and the viscosity of the extrudate
5. 100g of PHB was added to the machine, and automatic injection begins
6. Initially, the PHB pellets at the entry the extruder screw are not melted enough to enter as quickly as necessary, and consequently startup requires extrusion occurs for a few minutes without drawing any polymer into the compression chamber
7. Automatic injection continued until no more polymer remained in the machine

To reduce the time investment on this investigation, rheometry was only performed on every fifth sample, while FTIR was performed on every sample. FTIR results were correlated with rheometry results, as well as to the order in which they were produced, using the Pearson coefficientρ, which is the covariance of two sets of data X and Y, normalized by the standard deviation s_i of the two sets:

Equation A1: Pearson Correlation Coefficient

$$\rho = \frac{\sum(X_i - \bar{X})(Y_i - \bar{Y})}{s_x s_y}$$

For a meaningful relationship between two data sets to exist, the Pearson coefficient for the data must exceed a critical value related to the degree of significance (5% in this case) and the number of data points in each set. The critical values are shown in table A2 below.

Table A1: Pearson Coefficients for a Range of Data Sets

Number of data points	Critical value of ρ
1	.997
2	.950
3	.878
4	.811
5	.754
6	.707
7	.666
8	.632
9	.602
10	.576

Correlating FTIR to Complex Viscosity

Table A3, shows ranges where the Pearson coefficient correlating FTIR to complex viscosity was greater than the critical value, along with the types of bonds represented by these wavenumbers. Strangely, changes in C-O stretch intensity are not coupled with changes in acyl stretch intensity between 1700 and 1740 inverse centimeters, as would be the case if acyl substitution of some sort were occurring. It is conceivable that this is evidence of the McLafferty degradation mechanism, although the reaction should result in a C=C stretching vibration in between 1600 and 1700 cm-1. This presents a small chance that an indicator of degradation exists in the infrared spectrum, but the work was not pursued further.

Table A2: Ranges of High Correlation Between Complex Viscosity and FTIR

Range of Wavenumbers	Possible Vibration Modes	Significance
3003 - 2964	CH3 stretches	Elimination reaction, converting alkane to alkene; Carbon-carbon bond formation;
2897 - 2873	CH3, CH2 symmetric stretch	Inconclusive
1200 - 1170	Ester C-O stretch	Conversion from ester to acid and acrylate, corroborated by CH3 stretch band
1065 - 1050	Ether C-O stretch	Conversion from ester to acid

Correlation of Absorption to Production Sequence

FTIR was also correlated to the order in which samples were moulded, to determine if there was any consistent rate of change during injection, possibly due to degradation or gradual ejection of residual purge polymer. Tables A4, A5 and A6 shows the wavenumbers at which the Pearson coefficients exceeded critical values, along with the types of bonds represented by these wavenumbers. The results of this experiment are ambiguous: the presence of –OH stretches in all three experiments indicates that significant degradation has occurred to increase the number of hydroxyl groups present, but the other correlated vibrations suggest either transesterification or degradation.

Table A3: Correlation between production order and FTIR, first set

Range of Wavenumbers	Possible Vibration Modes	Significance
3798 - 3609	-OH stretches	Presence of moisture
2980 - 2945	CH3 asymmetric stretch, crystalline	C-C bond formation or elimination reaction
1888 - 1731	C=O stretch, not characteristic of PHB	Formation of an ester or an acid of unknown origin, possibly related to degradation
1451 - 1436	CH2 deformation	Formation of an alkene, through an elimination reaction
1363 - 1358	CH3 symmetric deformation	Inconclusive
1319 - 1293	C-O-C stretching mode, crystalline	Transesterification; Degradation reaction
1118 - 1059	C-O stretching mode	Transesterification
1044 - 1002	C-O stretching mode	Transesterification

Table A4: Correlation between production order and FTIR, second set

Range of Wavenumbers	Possible Vibration Modes	Significance
3756 - 3690	–OH stretches	Presence of moisture
3221 - 3007	Alkene stretch band, not correlated specifically to PHB	Possibly indicates presence of acrylates
2840 - 1804	No likely vibrational modes in this range (nitriles, alkynes and aromatics have sharp, local peaks in this range)	Inconclusive; Possible indication of inaccuracy of method
1711 - 1501	No vibrational modes in this range	Inconclusive
1381 - 1374	CH3 symmetric deformation	Inconclusive
1294 - 1275	C-O-C crystalline stretching mode	Possibly indicates change in crystallization, but this is unlikely

Table A5: Correlation between production order and FTIR, third set

Range of Wavenumbers	Possible Vibration Modes	Significance
3633 - 3385	-OH stretches; C=O overtone	Presence of moisture; acyl substitution
2273 - 1810	No vibrational modes in this range	Inconclusive
1726 - 1718	C=O stretches	Conversion from ester to carboxylic acid, possibly indicating degradation
1384 - 1355	CH3 symmetric deformation	Inconclusive
1302 - 1286	C-O-C stretch, but not in the known range for PHB	Possible transesterification
1136 - 1107	C-O stretch	Strengthens transesterification hypothesis
1044 - 1036	C-O stretch	

Appendix A5: Early Evidence of Effectiveness of Joncryl

Despite the lack of reliability of the Brabender, it was possible to produce some evidence of an increase in PHB complex viscosity due to the presence of Joncryl. In this experiment, an important change was made from previous protocols. In previous experiments, Joncryl had been dry-mixed with polymer pellets prior to being added to the mixing chamber, while in the newer protocol Joncryl was added to the mixing chamber once the PHB pellets had partially melted. Initially, the result seemed suspicious, and it was only when the experiment was repeated that the marginal gain in complex viscosity was accepted as real, and not an artifact caused by the unreliability of the method. The results are shown in Figure A7. This was the first, albeit extremely marginal, increase in PHB complex viscosity recorded as part of this project. When the Haake and its promise of reproducible results became available, this result formed the justification for continuing to investigate the reaction of PHB and Joncryl.

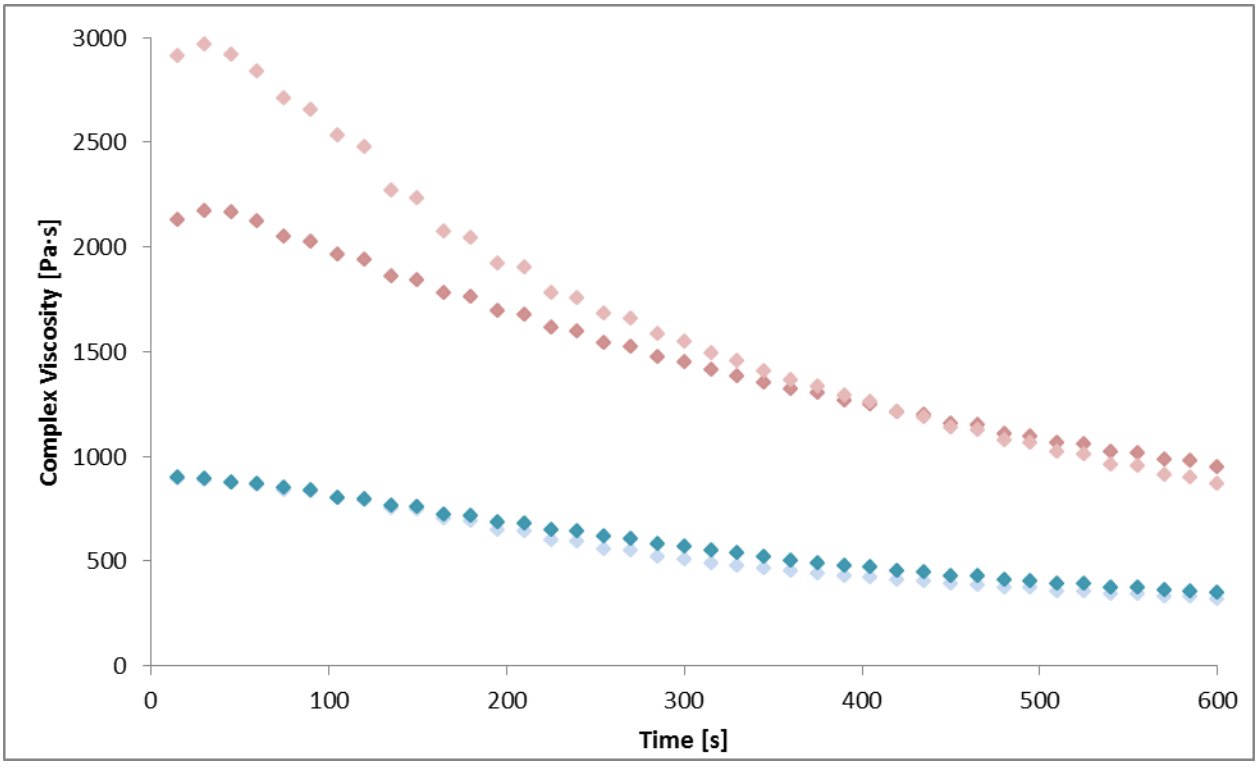

Figure A7: Complex Viscosity of Neat PHB (blue data) and Joncryl-loaded PHB (red data) from two different non-consecutive compounding sessions. Light blue and red data from September 6, 2012; Dark blue and red from October 15, 2012

Appendix A6: Co-continuity of 50% PHB/50% PLA from Micrographs

While studying the complex viscosity of PHB/PLA blends, the behavior of the 50% PHB/50% PLA blend was found to be more complex and unpredictable than the complex viscosity of other blends. This was hypothesized to be due to differences in morphology. To investigate further, SEM images were taken of cryofractured blends. Shown in figure A8 are of a 50% PHB/50% PLA blend at magnifications of 500x, 1000x, and 3000x, along with images of the 75% PHB/25% PLA blend at the same magnifications. Clearly, the morphology of the 50% PHB/50% PLA blend is not a simple droplet-matrix morphology.

It should be noted that the area of the 50% PHB/50% PLA fracture surface covered by droplets was 10% with an average droplet diameter of 2 μm, while the area of the 75% PLA/25% PHB fracture surface covered by droplets was 17% with an average diameter of 6 μm.

Of course, fracture surfaces are not preferable for any quantitative study of morphology because the shape of the surface is not controlled and because the fracture tends to form at weak points in the sample, where the morphology is not necessarily a good representation of the whole. Microtomed samples are preferred, because the surface is smooth and because it is not dictated by flaws in the material.

Some attempts were made to investigate microtomed samples, but the microtome blade tended to smear PHB across the surface of the sample, even under liquid nitrogen. The blends were etched by vapors from solvents which were intended to selectively dissolve one phase, in the hope of developing a better image. Solvents included toluene, acetone, methanol and chloroform. A few milliliters of the solvent was poured into the bottom of a container in which a cryofractured or microtomed sample was also placed and the container was closed to allow vapor-liquid equilibrium to be established. The sample surface was exposed to the vapor for periods between 2 and 45 minutes before being removed. Unfortunately, the images of these surfaces did not show anything that was deemed useful.

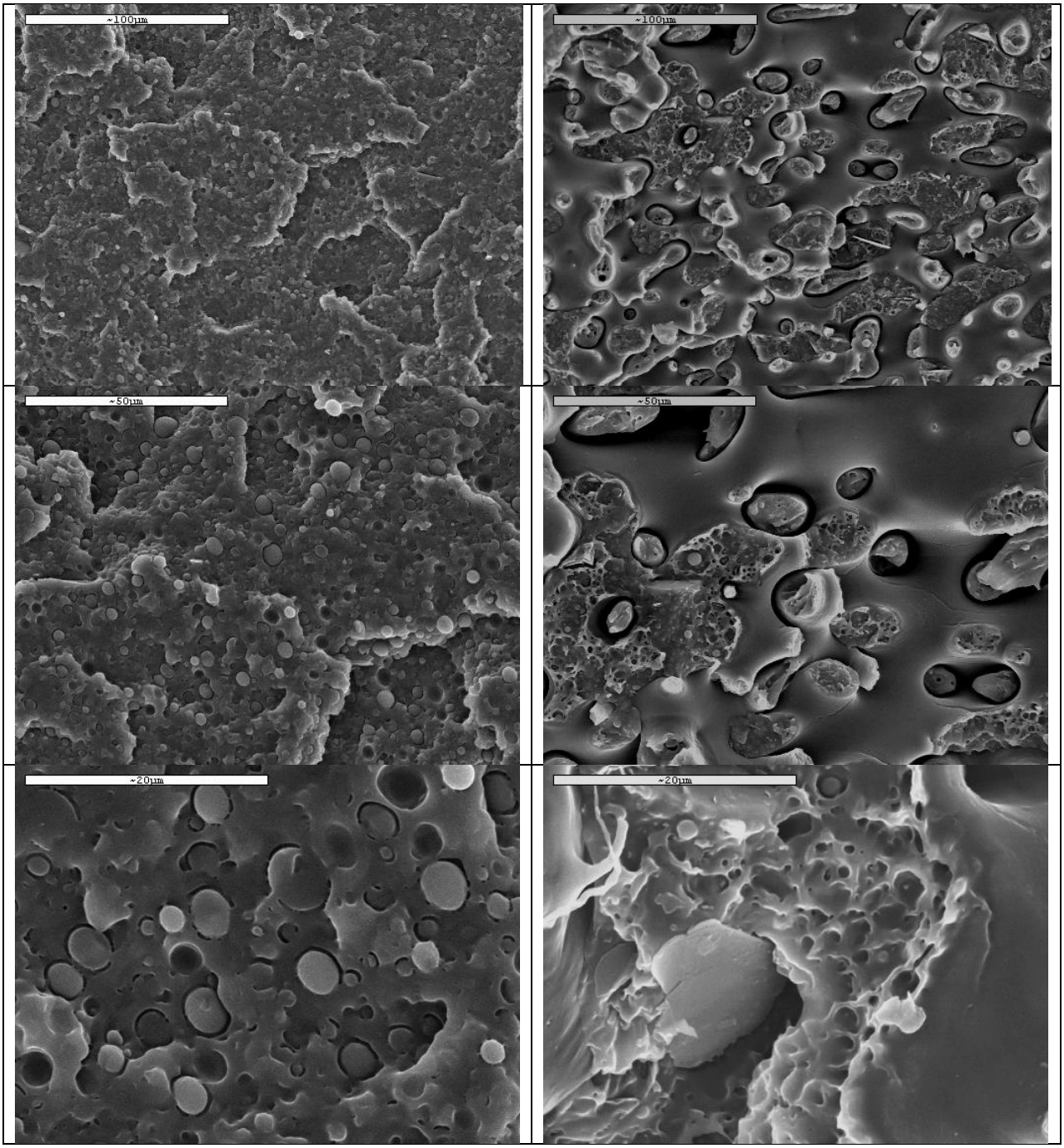

Figure A8: SEM images of 75% PHB/25% PLA (left) and 50% PHB/50% PLA (right), at magnifications of 500x (top), 1000x (middle), 3000x (bottom)

Appendix A7: Storage and Loss Moduli of PLA, Neat and with 1% Joncryl

As noted in the results section, the brittleness of Joncryl-loaded PLA suggests that it may have crosslinked. During time-sweeps, storage and loss modulus were taken in addition to complex viscosity. The average of storage and loss moduli for PLA, both neat and with 1% Joncryl are displayed in Figure A9, below. Even with 1% Joncryl, the loss modulus is still higher than storage modulus, indicating a lack of crosslinking. However, the increase in storage modulus for this sample is still significantly greater than that experienced by any other blend.

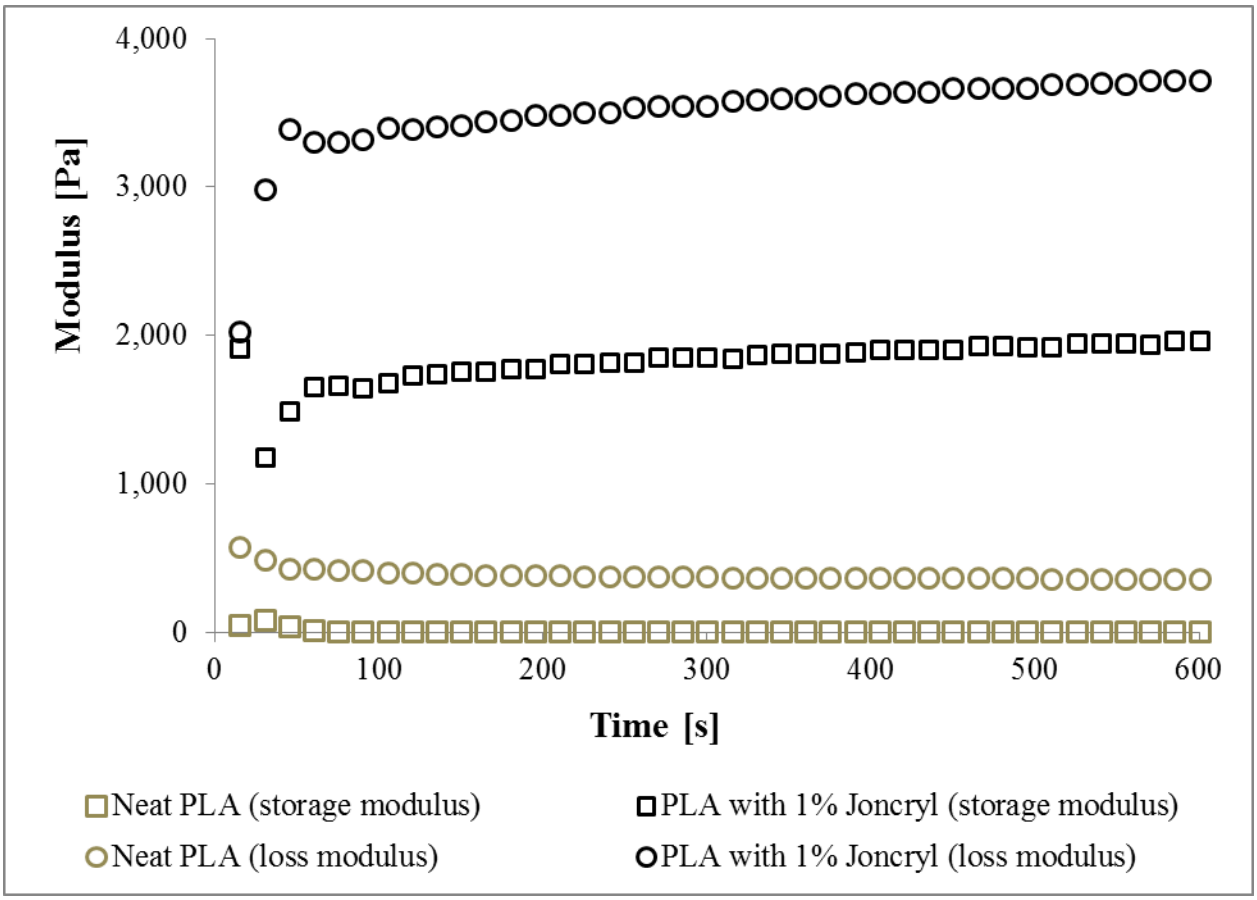

Figure A9: Storage and loss moduli for neat PLA and PLA with 1% Joncryl

Appendix A8: Other PHB/PLA Complex Viscosity Investigations

As detailed in Figure A10, the behavior of the 50% PHB/50% PLA blend was curious and merited further study. Consequently, an experiment was performed in which a number of blends were produced with compositions close to 50% PHB/50% PLA, to determine if any kind of trend or discontinuity could be observed in their behavior. The blend compositions were: 40% PHB/60% PLA, 45% PHB/55% PLA, 50% PHB/50% PLA, 55% PHB/45% PLA and 60% PHB/40% PLA. The result of this experiment is shown in the graph below. Unfortunately, a clear trend is not visible – the plots all seem to follow the same trend with only marginal differences in magnitude.

Along with the 50/50 region, the PLA-rich blends seemed to merit additional investigation, based on the extent to which they had been covered in literature, with reports of synergies in mechanical properties and some suggestion of interaction at very low concentration of PHB. Consequently, blends were prepared at compositions of 15% PHB/85% PLA and 35% PHB/65% PLA, and these blends were compared to the 25% PHB/75% PLA blend as well as to PLA as a homopolymer. Due to concerns with reproducibility, the results were redone, with both sets of data presented in Figure A11. The results for the 35% PHB/65% PLA were not consistent, and it is uncertain which result represents the truth. While it is difficult to draw conclusions from this graph (and in hindsight it is difficult to understand why it was done at all), it is interesting the 15% PHB/85% PLA curves, as well as one of the 25% PHB/75% PLA curve, have effectively the same complex viscosity as the PLA homopolymer.

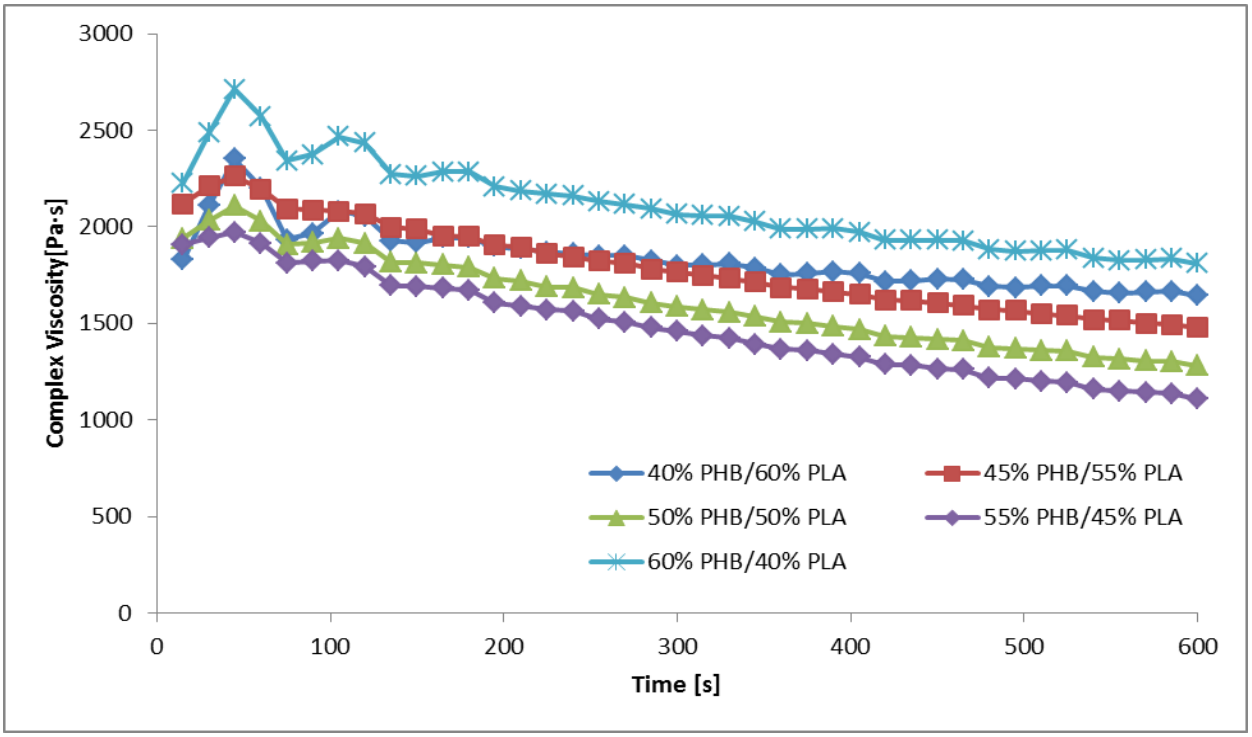

Figure A10: Complex viscosity of PHB/PLA blends in the vicinity of 50% PHB/50% PLA

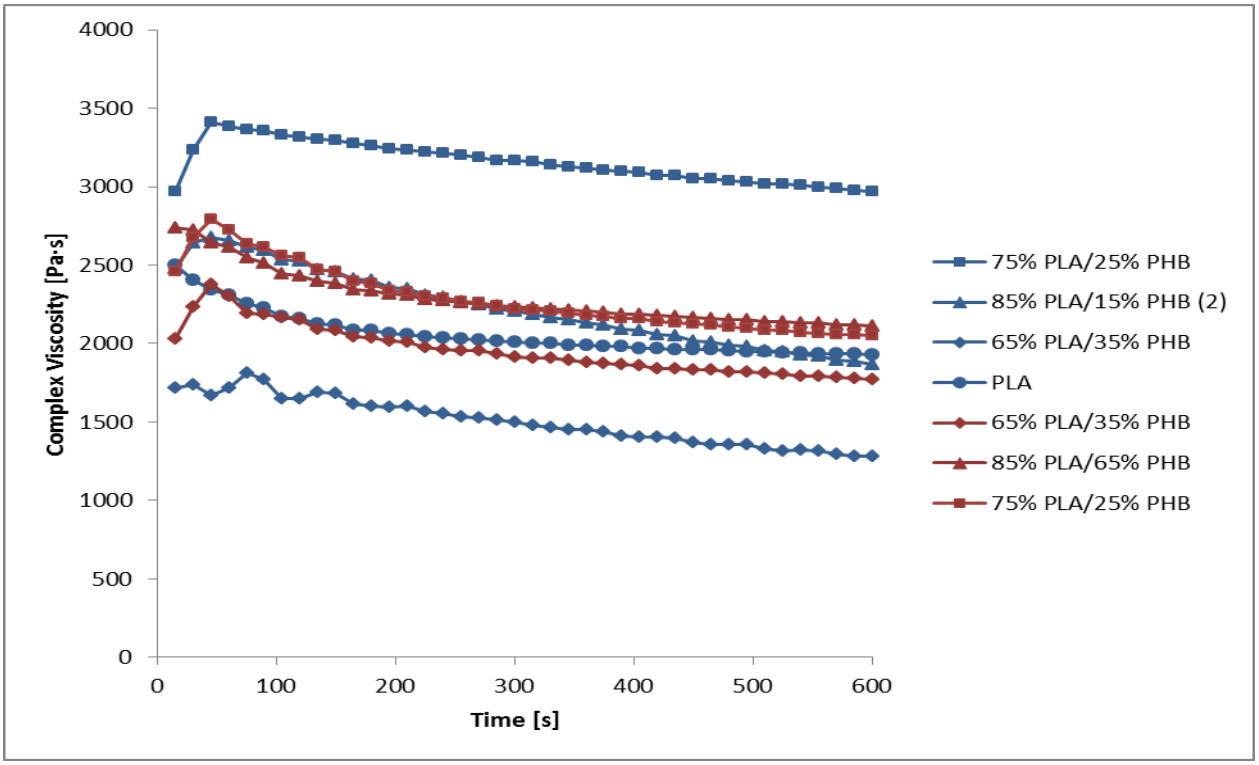

Figure A11: Complex viscosity for 65% PLA/25% PHB (diamond icons), 75% PLA/25% PHB (squares), 85% PLA/ 15% PHB (triangles) and PLA (circles) produced in two different sets of consecutive compounding sessions. Colours (blue and red) indicate data produced in consecutive compounding sessions